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PROFESSOR V. L. OMELIANSKY

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FIELD EXPERIMENTS ON THE AVAILABILITY OF NITROGENOUS FERTILIZERS, 1923-1927

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New Jersey Agricultural Experiment Station

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The field experiment on the availability of nitrogenous fertilizers, which was begun in 1908, has now been under way for 20 years. The results for the first 15 years have been presented in earlier papers (1, 2, 3). Beginning with 1923 certain modifications, referred to later, were made in the plans. In considering the results for the 5 years, 1923-1927, these modifications should be borne in mind. The experiment embraces forty $\frac{1}{10}$ -acre plots, half of which receive lime at intervals of 5 years (2 tons ground limestone to the acre) and half receive no lime. The fertilizer treatment is the same for both sections, that is, a given plot in the unlimed section (A) receives the same fertilizer treatment as a corresponding plot in the limed section (B). The following outline indicates the fertilizer treatment which was followed previous to 1923.

PLOT NUMBER	FERTILIZER TREATMENT FOR $\frac{1}{10}$ -ACRE PLOT
1A, 1B	Nothing
2A, 2B	16 pounds muriate of potash
3A, 3B	32 pounds acid phosphate
4A, 4B	Minerals only*
5A, 5B	Minerals, 1600 pounds cow manure
6A, 6B	Minerals, 1600 pounds horse manure
7A, 7B	Nothing
8A, 8B	Minerals, 8 pounds NaNO_3
9A, 9B	Minerals, 16 pounds NaNO_3
10A, 10B	Minerals, $\text{Ca}(\text{NO}_3)_2$ equivalent to 16 pounds NaNO_3
11A, 11B	Minerals, $(\text{NH}_4)_2\text{SO}_4$ equivalent to 16 pounds NaNO_3
12A, 12B	Minerals, CaCN_2 equivalent to 16 pounds NaNO_3
13A, 13B	Minerals, dried blood equivalent to 16 pounds NaNO_3
14A, 14B	Minerals, fish equivalent to 16 pounds NaNO_3
15A, 15B	Minerals, concentrated tankage equivalent to 16 pounds NaNO_3
16A, 16B	Minerals, 200 pounds alfalfa hay
17A, 17B	Minerals, 200 pounds wheat or rye straw
18A, 18B	Minerals, 1600 pounds cow manure and 16 pounds NaNO_3
19A, 19B	Minerals only
20A, 20B	Minerals, 200 pounds wheat or rye straw and 16 pounds NaNO_3

* Minerals—32 pounds acid phosphate and 16 pounds muriate of potash.

The changes that were made beginning with 1923 were as follows:

1. The applications of superphosphate and muriate of potash were reduced to one-half of the original amount, that is, the amount became 320 pounds and 160 pounds to the acre respectively instead of 640 and 320 pounds.

2. The use of horse manure on plots 6A and 6B was discontinued so that a study might be made of the residual effect of the manure which had been applied up to this time.

3. Alfalfa and rye straw—plots 16A and B and 17A and B—were applied for the corn crop of 1923 but were not applied after this. The use of these materials was discontinued for the purpose of studying the residual effect of the organic matter.

4. After 1924 plots 13A and 13B, which formerly received nitrogen in the form of dried blood, received no nitrogen, the object in this case being to study the residual effect of the blood.

5. Plots 14A and 14B received the standard amount of nitrogen in the form of dried fish for the season of 1923; in 1924 and again in 1925 they received no nitrogen; beginning with 1926 they received the standard amount of nitrogen in the form of nitrate of soda and ammonium sulfate—half the nitrogen from each.

The soil is a Sassafras loam which in some places contains much fine gravel. This lack of uniformity is indicated by variations in the nitrogen content of samples from some of the plots.

The standard nitrogen application for the commercial materials is at the rate of 49.6 pounds of nitrogen per acre (320 pounds nitrate of soda, 15.5 per cent nitrogen). Where manure and manure and nitrate are used, the amount of nitrogen applied is much greater. Where the alfalfa and rye straw are used, the amount varies according to the composition of these materials.

Fertilizers and manure (and likewise alfalfa and rye straw when they were used) are applied annually a short time before putting in the seed with the exception that in the case of fall-seeded crops, only one-fourth of the mineral nitrogenous fertilizer in each case is applied at the time of seeding, the remaining three-fourths being applied as a top dressing the following spring.

The rotation for the first 5 years was 1 year of corn, 2 years of oats, 1 year of wheat, and 1 year of timothy. Beginning with 1913 the rotation was changed so that there was 1 year each of corn, oats, and wheat and 2 years of timothy. It will be noted that the rotation includes no legume crops. This is necessary in a study of the availability of commercial nitrogenous materials. It should be explained here, however, that the results on the limed plots for the past 10 years or more, have been very materially modified by the appearance on these plots of volunteer clover during the years when they were in timothy. At the end of the first 5-year period an attempt was made to measure the influence of this clover by digging it out, drying, and weighing it, and determining its content of nitrogen. At best this was only a partial correction, for it is impossible to get it all out. Since that time the clover has grown so profusely that no attempt has been made to make a correction in this manner. Careful notes have been made on its appearance in the various plots, but this cannot tell the whole story. Its appearance is due to the fact that where mineral fertilizers and lime are used in liberal amounts, the conditions are made especially favor-

able for clover, and when the seeds become scattered only cultivation will prevent its growing if the supply of available nitrogen is limited. During the seasons of 1926 and 1927 it grew luxuriantly on the check plots of the limed section (minerals and lime without nitrogen), and the timothy was very much suppressed.

The fact that clover was present on these plots is indicated by the weight of the hay and also especially by the higher percentage of nitrogen in the hay.

On the other hand there was practically no clover on the unlimed section where the soil is distinctly acid (pH about 5.0-5.5). In this connection mention may be made of the fact that certain wild plants such as daisies (*Chrysanthemum leucanthemum*), dog fennel (*Anthemis cotula*), and wild carrot (*Daucus carota*) made their appearance in the plots on the limed section (pH 6.8-7.2) to a considerable extent, but were practically absent from the plots of the unlimed section. Sheep sorrel (*Rumex acetosella*) grew quite abundantly at certain times on the unlimed plots. On plot 11A where the soil has become very acid through the continued use of sulfate of ammonia without lime, it is practically the only plant that will grow during the early part of the season, whereas crab grass (*Digitaria* sp.) makes abundant growth in the late summer and fall.

The results of the work for the fourth 5-year period are discussed in the following pages.

YIELD OF DRY MATTER

A. Unlimed section

The yields of dry matter for both the unlimed and limed sections are set forth in table 1.

It is significant that plot 3A—superphosphate only—consistently gave larger yields than 2A, which receives muriate of potash only. This would indicate that the crops grown on this soil respond to phosphate treatment rather than to potash treatment. Indeed 2A with muriate of potash shows a lower total yield for the 5 years than 1A which receives nothing. The yields from 4A and 19A are averaged for the check, these plots having received phosphate and potash but no nitrogen. Plot 5A shows distinctly the effect of the heavy applications of manure. In 1927 there was a heavy second crop of timothy which ran the total yield for that year up to $3\frac{1}{2}$ tons to the acre. The total for the 5 years, for this plot, is over 14 tons to the acre, the second largest yield for the entire section.

It will be recalled that beginning with 1923 the manure was discontinued from plot 6A, but the yield of corn for that year was, with one exception, the largest of any. However, from this time on the yields gradually declined so that the total for the 5 years falls short of the total for plot 5A by nearly 7000 pounds. Here we have a good illustration of what happens when an acid soil is allowed to become deficient in nitrogen and organic matter (and not many years are required for this). Were this same soil limed, clover would steal in

TABLE I
Yield of dry matter—5-year period, 1923–1927
(Calculated to acre basis)

PLATE NUMBER	FERTILIZER TREATMENT (AS REVISED, 1923–1927)	CORN—1923			OATS—1924			WHEAT—1925			TIMOTHY— 1926			TIMOTHY— 1927			TOTAL INCREASE OVER CHECK	
		Grain	Stalks	Cobs	Grain	Straw		Grain	Straw		Grain	Straw		Grain	Straw			
1A	Nothing.....	1,733	1,860	350	695	934		740	1,189	1,217		638		9,356		Loss		
2A	160 pounds muriate of potash.....	1,223	2,020	283	719	1,088		725	1,207	972		726		8,963		Loss		
3A	320 pounds superphosphate.....	1,930	2,000	418	794	1,183	1,118	1,868	1,605			793		11,709		Loss		
4A	Minerals only*.....	1,795	2,520	323	902	1,591	1,298	2,498	1,219			471		12,617†		Check		
5A	Minerals and 16 tons cow manure.....	2,775	2,900	433	1,423	2,778	1,733	5,518	3,277			7,516†		28,353	16,360			
6A	Minerals only.....	3,083	2,960	458	1,198	2,496	1,722	4,673	2,127			2,942		21,659	9,666			
7A	Nothing.....	695	850	165	145	247	127	266	43			118		2,656		Loss		
8A	Minerals and 160 pounds NaNO ₃	1,645	2,700	260	895	1,794	1,303	3,925	1,488			1,711		15,721	3,728			
9A	Minerals and 320 pounds NaNO ₃	2,180	2,740	353	1,194	2,853	1,438	4,825	2,797			4,699		23,079	11,086			
10A	Minerals and Ca(NO ₃) ₂ equivalent to 320 pounds NaNO ₃	2,023	2,740	360	1,176	2,698	1,401	4,704	2,772			4,325		22,199	10,206			
11A	Minerals and (NH ₄) ₂ SO ₄ equivalent to 320 pounds NaNO ₃	758	840	155	389	1,128	101	350			2,150†		5,871		Loss		
12A	Minerals and CaCN ₂ equivalent to 320 pounds NaNO ₃	2,573	3,180	475	1,207	2,473	1,879	4,276	3,443			3,323		22,829	10,836			
13A	Minerals only.....	2,603	3,200	488	777	1,669	1,134	2,067	1,690			1,130		14,758	2,765			
14A	Minerals and NaNO ₃ , (NH ₄) ₂ SO ₄ (N half and half).....	3,000	2,680	498	1,034	1,912	1,428	2,861	4,099			Sample		17,512	5,519			
15A	Minerals and tankage equivalent to 320 pounds NaNO ₃	2,425	3,220	428	856	1,551	1,020	3,025	1,192			lost						
16A	Minerals only.....	2,808	2,680	420	839	1,351	1,267	3,140	1,115			2,081		15,798	3,805			
17A	Minerals only.....	1,295	2,760	230	832	1,267	1,264	2,881	959			954		14,574	2,581			
18A	Minerals and 16 tons manure and 320 pounds NaNO ₃	3,175	3,680	540	1,481	2,317	1,574	6,664	5,559**			578		12,066	73			
19A	Minerals only.....	1,650	3,100	280	669	1,226	1,043	2,098	723			7,232†		32,222	20,229			
20A	Minerals and 2 tons rye straw and 320 pounds NaNO ₃	2,750	2,840	463	1,125	2,108	906	3,763	3,711			579		11,368†	Check			
Average.....		2,106	2,574	369	918	1,733	1,161	3,090	2,000			2,328		16,278	7,651			

AVAILABILITY OF NITROGENOUS FERTILIZERS

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1B	Nothing.....	2,078	2,340	160	547	766	754	1,357	820	617	9,439	Loss
2B	160 pounds muriate of potash.....	2,703	2,640	478	690	1,006	1,007	1,923	1,074	869	12,390	Loss
3B	320 pounds superphosphate.....	1,975	2,580	370	585	829	842	1,365	850	623	10,019	Loss
4B	Minerals only*.....	2,600	3,700	410	635	993	985	2,190	836	2,102	14,451†	Check
5B	Minerals and 16 tons cow manure.....	2,383	3,700	395	1,011	2,046	2,263	747	1,697	3,824†	20,029	4,538
6B	Minerals only.....	3,200	4,040	523	866	1,844	1,382	3,292	1,102	2,547	18,796	3,305
7B	Nothing.....	2,248	2,900	418	529	796	982	1,864	667	1,037	11,441	Loss
8B	Minerals and 160 pounds NaNO ₃	2,780	3,460	443	977	1,904	1,444	3,597	1,668	2,998	19,271	3,780
9B	Minerals and 360 pounds NaNO ₃	2,250	3,320	398	1,001	2,194	1,499	4,537	2,906	4,177	22,282	6,791
10B	Minerals and Ca (NO ₃) ₂ equivalent to 320 pounds NaNO ₃	3,105	3,660	508	1,124	2,729	1,742	5,278	3,778	4,368	26,292	10,801
11B	Minerals and (NH ₄) ₂ SO ₄ equivalent to 320 pounds NaNO ₃	2,800	3,180	460	1,130	2,678	1,735	4,768	2,998	3,888	23,637	8,146
12B	Minerals and CaCN ₂ equivalent to 320 pounds NaNO ₃	3,000	3,280	478	1,173	2,333	1,849	5,144	3,097	3,528	23,882	8,391
13B	Minerals only.....	2,970	3,200	475	780	1,565	1,357	2,938	1,951	2,303	17,539	2,048
14B	Minerals and NaNO ₃ , (NH ₄) ₂ SO ₄ (N half and half).....	2,925	3,380	490	813	1,570	1,274	2,960	1,136	4,431	20,979	5,488
15B	Minerals and tankage equivalent to 320 pounds NaNO ₃	2,758	3,980	488	1,264	2,698	1,493	4,135	1,852	2,924	21,592	6,101
16B	Minerals only.....	2,983	2,680	450	826	1,731	1,432	3,615	1,280	3,055	18,052	2,561
17B	Minerals only.....	2,653	3,720	473	859	1,361	1,405	3,439	1,298	6,287†	21,505	6,014
18B	Minerals and 16 tons manure and 320 pounds NaNO ₃	3,413	3,840	570	1,356	2,353	1,583	5,908	4,970**	7,867†	31,865	16,374
19B	Minerals only.....	2,405	3,220	418	674	1,041	1,127	2,548	988	4,110†	16,531†	Check
20B	Minerals and 2 tons tire straw and 320 pounds NaNO ₃	2,113	3,180	375	1,101	1,940	929	3,755	3,330	4,417	21,140	5,649
	Average.....	2,667	3,300	439	898	1,719	1,303	3,418	2,015	3,299	19,057	6,428

* Minerals = 160 pounds muriate of potash and 320 pounds superphosphate.

** 18A, credit 1298 pounds of the total for this year to second cutting of hay.

18B, credit 1168 pounds of the total for this year to second cutting of hay.

† 5A, credit 1979 pounds of the total for this year to second cutting of hay.

11A, credit 1947 pounds of the total for this year to second cutting of hay.

18A, credit 2377 pounds of the total for this year to second cutting of hay.

5B, credit 1062 pounds of the total for this year to second cutting of hay.

17B, credit 2180 pounds of the total for this year to second cutting of hay.

18B, credit 2335 pounds of the total for this year to second cutting of hay.

19B, credit 914 pounds of the total for this year to second cutting of hay.

† Averaged for check.

and help to save the situation, but this cannot happen so long as the soil is sharply acid.

Plot 7A, which receives no fertilizer or manure, cannot be compared with 1A because at this point the soil is poorer and contains more gravel than at the location of 1A. The yields on 7A have declined rapidly and of late years have almost failed. The total yield on this plot for the 5 years amounts to a little more than a ton and a half of dry matter to the acre. The total 5-year yield for 8A is at the rate of 15,721 pounds per acre as against 23,079 pounds for 9A, the difference in treatment being that 8A receives nitrate of soda at the rate of 160 pounds per acre annually and 9A nitrate of soda at the rate of 320 pounds per acre. It is very evident that the larger application is fully justified. The increase in yield would much more than pay for the additional nitrate of soda. Plot 10A with nitrate of lime gave yields only slightly less than 9A, which receives its nitrogen in the form of nitrate of soda.

As previously stated plot 11A which receives ammonium sulfate and no lime, has become so acid that it supports little vegetation other than sheep sorrel (*Rumex acetosella*) and crab grass (*Digitaria* sp.). In the fall of 1927 there was a heavy growth of the latter amounting to 1947 pounds of dry matter. The yields on 12A with calcium cyanamid have been well maintained, being only slightly less than the yields with nitrate of soda. Apparently the calcium cyanamid has had no toxic effect though used in larger amounts than is generally recommended. The yields from 13A have declined since the applications of nitrogen (dried blood) have been discontinued, the total yield for the period 1923 to 1927 being at the rate of 14,758 pounds to the acre, whereas the total yield for the period 1918-1922 was at the rate of 16,419 pounds to the acre. With the change from fish scrap to nitrate of soda and ammonium sulfate, plot 14A, yields have increased, though unfortunately this plot received no nitrogen for the crops of 1924 and 1925. Plot 16A, without nitrogen during the past 5 years, shows some decrease in yield. The timothy crops of 1926 and 1927 were especially small. Plot 17A, also without nitrogen for the 5 years, shows a slight increase over the previous 5 years though the timothy crops of 1926 and 1927 were small.

The total yield on 18A—32,222 pounds per acre—is about 10,000 pounds in excess of the total yield on this plot during the third 5-year period. This furnishes a good illustration of the cumulative effect of heavy applications of manure when used in combination with mineral fertilizers. It will be noted that this plot yielded heavy second cuttings of hay in 1926 and 1927. Plots that receive only the standard application of nitrogen did not yield a second cutting of hay. The yields for 20A are also somewhat in excess of the yields for this plot during the third 5-year period. This plot receives nitrogen in the form of nitrate of soda and also a small amount in the form of rye straw but the nitrogen in the latter is very slowly available.

B. Limed series

In total yields of dry matter the limed plots do not differ widely from the unlimed plots. This is in accord with results previously reported and is not difficult to understand when it is remembered that the crops constituting the rotation are all non-legumes. It is true, as previously explained, that volunteer clover appeared in some of the B plots, but only on a few of these was the yield of clover large enough materially to affect the total yields. It is already well known that generally speaking the non-legume crops are less affected by an acid soil than are the legume crops.

There are a number of points of interest in connection with the yields from these plots. For example, plot 3B, which receives superphosphate only, gave a lower total yield than 2B, which receives muriate of potash only. This, it will be noted, is the reverse of what happened on the unlimed section. The total 5-year yield on 3B is decidedly less than the total yield on the corresponding unlimed plot. It is possible that this difference should be attributed to the weeds which grew rather profusely on this plot, the lime treatment seeming to favor these plants. Plot 6B also gave a smaller yield than 6A. This no doubt is due in part to the fact that plot 6B lies along the edge of the road next to the woods and yields may have been adversely influenced by these conditions. Plot 7B gave very much larger yields than 7A. This is due to two causes: 1. The soil in this part of the field is better than the soil in that part of the field where 7A is located, and 2. The lime which has been applied to 7B has encouraged the growth of some clover. It is noteworthy, however, that because of the lack of phosphate and potash the volunteer clover did not make very much headway on this plot. This is shown by the percentage of nitrogen in the hay.

It is of interest to note that the additional 160 pounds per acre of nitrate of soda which plot 9B gets over 8B did not make the difference that was noted in the corresponding unlimed plots. This can be readily understood when it is remembered that a deficient supply of nitrogen where there is an abundant supply of lime and mineral fertilizers (plot 8B) encourages the growth of volunteer clover which in turn suppresses or crowds out the timothy. Plot 10B shows the highest total yield of any of the plots that receive commercial nitrogenous materials. The total yields from plots 11B and 12B are very nearly the same, and are only a little more than the total for 9B. The figures for 11B furnish abundant proof that when lime is supplied in adequate amounts, ammonium sulfate has no injurious or depressing effect. The hydrogen-ion concentration of the soil from 11B is pH 6.5 whereas the concentrations for 9B and 10B are pH 7.1 and 7.3 respectively.

The lack of available nitrogen has undoubtedly influenced the yield from plot 13B, which is decidedly less than the yields from the plots on either side. On account of the nitrogen deficiency there was considerable volunteer vetch and clover on this plot. This is shown by the higher percentage of nitrogen in

the hay. The total 5-year yield for plot 14B shows a considerable increase over the total yield for the previous 5-year period. The yields on 16B and 17B have been well maintained considering the fact that no nitrogen has been applied since 1922. The explanation for the good yields is again to be found in the volunteer clover already mentioned. In 1927 the growth of clover on plot 17B was especially heavy as indicated by the percentage of nitrogen in the hay. Plot 18B gave a second cutting of timothy in 1926 and also in 1927, the latter being at the rate of more than a ton to the acre. The total yield for the 5 years is slightly less than the total yield for the corresponding unlimed plot (18A). It is nearly 3 tons more than the yield for the 5-year period 1918-1922. Plot 20B also shows some increase over the preceding 5-year period, but the yield is slightly less than on the corresponding unlimed plot 20A.

TABLE 2
Percentage of nitrogen in the crops—5-year period, 1923-1927

PLOT NUMBER	CORN—1923			OATS—1924		WHEAT—1925		TIMOTHY —1926	TIMOTHY— 1927
	Grain	Stalks	Cobs	Grain	Straw	Grain	Straw		
	per cent	per cent	per cent	per cent	per cent	per cent	per cent		per cent
1A	1.221	0.221	0.219	2.015	0.475	2.236	0.436	0.980	0.795
2A	1.137	0.505	0.213	1.970	0.397	2.152	0.445	1.098	0.858
3A	1.253	0.609	0.251	1.998	0.380	1.997	0.290	0.797	0.917
4A	1.175	0.562	0.235	1.970	0.345	1.786	0.318	0.775	0.877
5A	1.763	0.899	0.376	2.427	0.475	2.208	0.366	0.814	0.817†
6A	1.607	0.956	0.291	2.261	0.468	2.068	0.394	0.804	0.771
7A	1.394	0.789	0.282	2.163	0.891	2.363	0.698	1.133	0.826
8A	1.466	0.578	0.276	2.244	0.411	2.307	0.422	0.779	0.645
9A	1.607	0.767	0.266	2.349	0.564	2.222	0.450	0.886	0.573
10A	1.591	0.710	0.266	2.304	0.447	2.062	0.473	0.908	0.621
11A	1.472	0.899	0.266	2.138	1.000	2.644	0.754	1.251†
12A	1.497	0.679	0.235	2.209	0.465	2.034	0.324	0.873	0.608
13A	1.597	0.656	0.282	1.864	0.455	1.949	0.253	0.793	0.810
14A	1.544	0.751	0.251	2.138	0.465	1.935	0.324	0.748	Sample lost
15A	1.535	0.688	0.282	2.103	0.473	2.470	0.464	1.070	0.736
16A	1.597	0.925	0.251	2.093	0.429	2.011	0.318	0.877	0.799
17A	1.253	0.489	0.219	1.829	0.309	2.034	0.360	0.790	0.793
18A	1.723	0.899	0.307	2.596	0.873	2.864	0.521	0.873*	0.880†
19A	1.300	0.852	0.251	1.899	0.436	2.011	0.332	0.952	0.987
20A	1.566	0.420	0.260	2.138	0.447	2.250	0.529	0.775	0.547
Average...	1.464	0.693	0.264	2.135	0.510	2.180	0.424	0.880	0.795
1B	1.294	0.530	0.251	2.054	0.527	2.138	0.487	1.091	0.734
2B	1.347	0.546	0.235	2.036	0.382	1.992	0.352	0.777	0.964
3B	1.247	0.505	0.219	2.018	0.400	1.911	0.352	0.793	0.667
4B	1.748	0.584	0.298	1.974	0.356	1.911	0.296	0.756	1.176
5B	1.770	0.947	0.307	2.338	0.636	2.358	0.360	0.793	0.669†
6B	1.535	0.641	0.266	2.217	0.510	2.099	0.304	0.748	0.722
7B	1.237	0.514	0.213	2.129	0.616	1.862	0.282	0.921	0.602

TABLE 2—Continued

PLOT NUMBER	CORN—1923			OATS—1924		WHEAT—1925		TIMOTHY —1926	TIMOTHY— 1927
	Grain	Stalks	Cobs	Grain	Straw	Grain	Straw		
	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent
8B	1.629	0.625	0.260	2.041	0.422	1.905	0.304	0.744	0.724
9B	1.660	0.726	0.278	2.316	0.598	2.283	0.388	0.775	0.610
10B	1.535	0.663	0.246	2.217	0.528	2.122	0.403	0.672	0.561
11B	1.513	0.615	0.221	2.323	0.591	2.164	0.403	0.807	0.691
12B	1.613	0.830	0.237	2.129	0.563	2.147	0.374	0.694	0.574
13B	1.597	0.956	0.300	2.129	0.486	1.879	0.276	0.670	1.046
14B	1.597	0.726	0.309	2.104	0.475	1.927	0.304	0.672	0.621
15B	1.607	0.789	0.278	2.041	0.415	2.099	0.408	0.712	0.777
16B	1.716	1.199	0.268	2.104	0.433	1.943	0.332	0.734	1.092
17B	1.597	0.625	0.294	2.138	0.393	1.960	0.352	0.722	1.404†
18B	1.723	0.947	0.294	2.327	0.574	2.753	0.563	0.838*	0.887†
19B	1.519	0.836	0.262	2.054	0.382	2.860	0.338	0.779	1.290†
20B	1.597	0.925	0.268	2.109	0.411	2.429	0.600	0.790	0.724
Average...	1.554	0.736	0.265	2.140	0.485	2.137	0.374	0.774	0.827

* 18A, second crop contained 1.516 per cent nitrogen.

18B, second crop contained 1.762 per cent nitrogen.

† 5A, second crop contained 1.522 per cent nitrogen.

11A, second crop contained 0.920 per cent nitrogen.

18A, second crop contained 1.554 per cent nitrogen.

5B, second crop contained 1.619 per cent nitrogen.

17B, second crop contained 1.255 per cent nitrogen.

18B, second crop contained 1.617 per cent nitrogen.

19B, second crop contained 1.487 per cent nitrogen.

It is probable that could the clover have been entirely excluded from the limed plots the average yields would have been very close to the average yields for the unlimed section. The quality of the hay on the unlimed section was probably slightly superior to that on the limed section because the lime appeared to favor the growth of certain weeds.

PERCENTAGE OF NITROGEN IN THE DRY MATTER

The difference in the percentage of nitrogen in samples from the limed and unlimed sections is not great (see table 2). It may be noted, however, that wherever the treatment has been abnormal, the percentage of nitrogen is usually increased. For example, plots 18A and 18B receive an excessive amount of nitrogen and usually crop samples from these plots show a percentage of nitrogen considerably above the average. In 1925 the wheat from 18A showed 2.86 per cent nitrogen and from 18B 2.75 per cent nitrogen, where the average for all plots is 2.18 per cent. Plot 11A (which is highly acid) receives far more nitrogen than can be used by the small crops which it produces and the wheat grown on this plot for 1925 analyzed 2.65 per cent of nitrogen as

against an average of 2.18 per cent for all plots. In 1927 the timothy on this plot was a failure, but there was a heavy crop of crab grass (*Digitaria* sp.), the hay of which analyzed 1.25 per cent nitrogen as against an average of 0.8 per

TABLE 3
Yield of nitrogen—5-year period, 1923–1927
(Calculated to acre basis)

PLOT NUMBER	CORN—1923			OATS—1924		WHEAT—1925		TIMOTHY—1926	TIMOTHY—1927	TOTAL FOR 5 YEARS	INCREASE OVER CHECK
	Grain		Stalks	Cobs	Grain	Straw	Grain	Straw			
	lbs.	lbs.	lbs.	lbs.	.lbs.	lbs.	lbs.	lbs.			
1A	21.2	4.1	0.8	14.0	4.4	16.6	5.2	11.9	5.1	83.3	
2A	13.9	10.2	0.6	14.2	4.3	15.6	5.4	10.7	6.2	81.1	
3A	24.2	12.2	1.1	15.7	4.5	22.3	5.4	12.8	7.3	105.5	
4A	21.1	14.2	0.8	17.8	5.5	23.2	7.9	9.5	4.1	104.1†	Check
5A	48.9	26.1	1.6	34.5	13.2	38.3	20.2	26.7	75.4†	284.9	179.2
6A	49.5	28.3	1.3	27.1	11.7	35.6	18.4	17.1	22.7	211.7	106.1
7A	9.7	6.7	0.5	3.1	2.2	3.0	1.9	0.5	1.0	28.6	
8A	24.1	15.6	0.7	20.1	7.4	30.1	16.6	11.6	11.0	137.2	31.5
9A	35.0	21.0	0.9	28.1	16.1	32.0	21.7	24.8	26.9	206.5	100.8
10A	32.2	19.5	1.0	27.1	12.1	28.9	22.3	25.2	26.9	195.2	89.5
11A	11.2	7.6	0.4	8.3	11.3	2.7	2.6	...	20.5†	64.6	
12A	38.5	21.6	1.1	26.7	11.5	38.2	13.9	30.1	20.2	201.8	96.1
13A	41.6	21.0	1.4	14.5	7.6	22.1	5.2	13.4	9.2	136.0	30.3
14A	46.3	20.1	1.3	22.1	8.9	27.6	9.3	30.7	Sample lost	166.3	60.6
15A	37.2	22.2	1.2	18.0	7.3	25.2	14.0	12.8	15.3	153.2	47.5
16A	44.8	24.8	1.1	17.6	5.8	25.5	10.0	9.8	7.6	147.0	41.3
17A	16.2	13.5	0.5	15.2	3.9	25.7	10.4	7.6	4.6	97.6	
18A	54.7	33.1	1.7	38.5	20.2	45.1	34.7	56.9*	79.7†	364.6	258.9
19A	21.5	26.4	0.7	12.7	5.4	21.0	7.0	6.9	5.7	107.3†	Check
20A	43.1	11.9	1.2	24.1	9.4	20.4	19.9	28.8	25.1	183.9	78.2
Average§...	37.1	19.9	1.1	24.8	11.7	28.9	17.5	27.5	33.4	195.8	104.7
1B	26.9	12.4	0.4	11.2	4.0	16.1	6.6	9.0	4.5	91.1	
2B	36.4	14.4	1.1	14.1	3.8	20.1	6.8	8.3	8.4	113.4	
3B	24.6	13.0	0.8	11.8	3.3	16.1	4.8	6.7	4.2	85.3	
4B	45.5	21.6	1.2	12.5	3.5	18.8	6.5	6.3	24.7	140.6†	Check
5B	42.2	35.0	1.2	23.6	13.0	28.9	13.5	13.5	35.7†	206.6	43.5
6B	49.1	25.9	1.4	19.2	9.4	29.0	10.0	8.2	18.4	170.6	7.5
7B	27.8	14.9	0.9	11.3	4.9	18.3	5.3	6.1	6.2	95.7	
8B	45.3	21.6	1.2	19.9	8.0	27.5	10.9	12.4	21.7	168.5	5.4
9B	37.4	24.1	1.1	23.2	13.1	34.2	17.6	22.5	25.5	198.7	35.6
10B	47.7	24.3	1.3	24.9	14.4	37.0	21.3	25.4	24.5	220.8	57.7
11B	42.4	19.6	1.0	26.3	15.8	37.6	19.2	24.2	26.9	213.0	49.9
12B	48.4	27.2	1.1	25.0	13.1	39.7	19.2	21.5	20.3	215.5	52.4
13B	47.4	30.6	1.4	16.6	7.6	25.5	8.1	13.1	24.1	174.4	11.3
14B	46.7	24.5	1.5	17.1	7.5	24.6	9.0	21.1	27.5	179.5	16.4
15B	44.3	31.4	1.4	25.8	11.2	31.3	16.9	13.2	22.7	198.2	35.1

TABLE 3—*Concluded*

PLOT NUMBER	CORN—1923			OATS—1924			WHEAT—1925			TIMOTHY— 1926	TIMOTHY— 1927	TOTAL FOR 5 YEARS	INCREASE OVER CHECK
	Grain	Stalks	Cobs	Grain	Straw	Grain	Straw	Grain	Straw				
	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.
16B	51.2	32.1	1.2	17.4	7.5	27.8	12.0	9.4	33.4	192.0	28.9		
17B	42.4	23.3	1.4	18.6	5.4	27.5	12.1	9.4	85.0†	225.1	62.0		
18B	58.8	36.4	1.7	31.6	13.5	43.7	33.3	52.4*	86.8†	358.2	195.1		
19B	36.5	26.9	1.1	13.8	4.0	32.2	8.6	7.7	54.8†	185.6‡	Check		
20B	33.7	29.4	1.0	23.2	8.0	22.6	22.5	26.3	32.0	198.7	35.6		
Average§...	44.7	27.4	1.3	24.1	11.8	32.7	18.3	23.3	32.4	215.8	52.7		

* Plot 18A, credit 19.68 pounds of total N for this year to second cutting of hay.

Plot 18B, credit 20.58 pounds of total N for this year to second cutting of hay.

† Plot 5A, credit 30.12 pounds of total N for this year to second cutting of hay.

Plot 11A, credit 17.91 pounds of total N for this year to second cutting of hay, (crab grass).

Plot 18A, credit 36.94 pounds of total N for this year to second cutting of hay.

Plot 5B, credit 17.19 pounds of total N for this year to second cutting of hay.

Plot 17B, credit 27.36 pounds of total N for this year to second cutting of hay.

Plot 18B, credit 37.76 pounds of total N for this year to second cutting of hay.

Plot 19B, credit 13.59 pounds of total N for this year to second cutting of hay.

‡ Averaged for check.

§ Average of nitrogen treated plots (5A to 20A, with the exception of 6A, 7A, 13A, 16A, 17A and 19A).

Average of nitrogen treated plots (5B to 20B, with the exception of 6B, 7B, 13B, 16B, 17B and 19B).

cent nitrogen for the hay on all the other plots. Likewise in 1927 there was a heavy growth of volunteer clover on 17B and the hay from this plot analyzed 1.4 per cent nitrogen where the average for all the other plots was 0.83 per cent nitrogen. Plots 4B, 13B, 16B, and 19B also show the influence of the volunteer clover judging by the analysis of the hay.

YIELD OF NITROGEN

The yield of nitrogen for a given plot is determined by multiplying the total yield of dry matter for that plot by the percentage of nitrogen in the dry matter. As would be expected there are some rather wide variations in total yields (see table 3). Generally the averages for the limed section exceed those for the unlimed section. Plots like 5A, 5B, 18A, and 18B, which receive heavy applications of manure, return through the crop relatively large amounts of nitrogen. Plots like 7A and 11A, where the crop is very small, return only small amounts of nitrogen.

The yields from the unlimed plots with nitrate of soda, calcium nitrate, and calcium cyanamid average close to 200 pounds per acre for the 5 years, or about 40 pounds per acre per year. Plot 15A which receives the same amount of

nitrogen as shown above in the form of tankage, has returned an average of about 30 pounds per acre per year. This plot shows a total increase over the check of less than 50 pounds per acre, whereas plot 9A with the same amount of nitrogen in the form of nitrate of soda shows a total increase of slightly over 100 pounds per acre. Plot 18A has returned through the crops 364.5 pounds of nitrogen for the 5 years, but this return has been at great expense, since this plot has received nitrogen at the rate of more than 200 pounds annually for the 5 years, or a total of more than 1000 pounds per acre.

It is of interest to compare plot 17A with 17B. The soil on the former is acid and no clover grows on this plot. The soil of 17B has been kept near the neutral point, and as already pointed out, much volunteer clover has made its appearance whenever the land was in grain or hay and not under cultivation. This has greatly influenced the yields of nitrogen, thus the total 5-year yield for 17B is at the rate of 225 pounds of nitrogen per acre, which is equivalent to 45 pounds annually, whereas the total yield for 17A is only 97.6 pounds per acre or slightly less than 20 pounds annually. Plots 4B and 19B—the check plots for the limed section—were similarly influenced by the clover. This increase in nitrogen on the check plots, due to the clover, makes the increase due to the fertilizer treatment appear to be less than it really is. In other words the nitrogen accumulated by the clover increases the amount for the check and thereby proportionately decreases the amount returned in the crop as a result of the fertilizer. Plot 13A where nitrogen has been discontinued yielded 135.9 pounds of nitrogen. Plot 13B, which in the absence of commercial nitrogen has been influenced by the clover, yielded 174.4 pounds of nitrogen.

From these figures it is quite clear that if the clover and vetch could have been entirely excluded from the limed plots they would have returned very little more nitrogen through the crops than did the unlimed plots. It would appear that as far as general farm crops are concerned the all-important function of lime when used in connection with phosphate and potash is to bring the soil into a condition that will enable it to support legume crops, which in turn play a very large part in soil improvement. The experiment likewise furnishes abundant evidence that clover and other legume crops may easily be grown when the conditions are made favorable.

PERCENTAGE OF NITROGEN RECOVERED

The omission of nitrogen from certain of the plots, the failure of the crops on plot 11A, and the disturbing influence of the clover on certain of the B plots have all tended to lessen the value of the figures for the percentage of nitrogen recovered during the fourth 5-year period (table 4). It is noteworthy, however, that the average recovery for the 5 years comes fairly close to 30 per cent for both the limed and unlimed section (in making the averages, plots showing a loss have been omitted). The average for the first 5-year period, unlimed

section, was 26.5 per cent and for the limed section 30.6 per cent (table 5). In each section the recoveries for the second and third 5-year periods were less.

Plot 9A, which is unlimed, and receives nitrate of soda, showed an average recovery of 40.7 per cent for the 5 years. Plots 10A with nitrate of lime and

TABLE 4
Percentage of nitrogen recovered—5-year period, 1923–1927

PLOT NUMBER	CORN—1923	OATS—1924	WHEAT—1925	TIMOTHY—1926	TIMOTHY—1927	5-YEAR AVERAGE
	per cent	per cent	per cent	per cent	per cent	per cent
5A	21.07	14.06	27.90	11.87	30.89**	21.16
8A	7.42†	27.38	34.46*	13.79	24.68	25.08
9A	29.64	47.34	48.65	33.49	44.38	40.70
10A	20.79	43.84	43.57	34.27	44.23	37.34
11A	46.71†	2.14†	48.83†	No crop	4.80†
12A	38.19	35.28	45.44	44.13	30.81	38.77
14A	51.23	45.34	Sample lost	48.29
15A	36.88	9.44	19.56	9.23	20.97	19.22
18A	20.47	15.70	32.79	19.73**	26.66**	23.07
20A	21.94	19.98	16.12	31.73	11.86	20.33
Average...	30.03	26.63	33.56	27.06	29.31	30.44
			1925†			
5B	7.37	10.23	16.49	4.14	11.31**	9.91
8B	6.65	44.44	26.49*	21.77	64.03	32.68
9B	7.78§	39.01	53.47	31.27	39.62	40.84
10B	13.63	53.03	66.41	37.06	37.64	41.55
11B	7.02§	50.67	63.45	34.64	42.42	47.80
12B	20.81	42.64	67.82	29.19	29.07	37.90
14B	12.78	28.35	43.73	28.29
15B	21.49	40.42	46.19	12.46	34.05	30.92
18B	13.21	11.61	33.71	18.71**	28.72**	21.19
20B	3.55§	22.22	29.64	29.74	15.36	24.24
Average...	13.71	34.92	44.85	24.73	34.50	31.53

* Through an error in 1925 this plot received 16 pounds NaNO₃ instead of 8 pounds.

** Part of this nitrogen represents the second crop.

† Loss; omitted from average. In 1927 plot 11A yielded a late crop of crab grass which returned 17.91 pounds of nitrogen.

‡ The yield on plot 4 only was taken as the check for this year.

§ Loss; omitted from average.

12A with calcium cyanamid show slightly lower recoveries. The unlimed sulfate of ammonia plot shows a continuous loss. This is due to the fact that the soil is very acid and produces no crop or only a small fraction of a normal crop. The corresponding limed plot has continuously produced good crops and shows a 5-year average recovery of 47.8 per cent, the highest for this sec-

tion. The recovery with nitrate of soda on plot 9B, limed, is practically the same as that from the corresponding unlimed plot.

The low recovery for the corn on the limed section in 1923 (average 13.7 per cent) is to be attributed to the exceptionally high yields on the control or check plots for this year, and these high yields in turn are to be attributed to the volunteer clover which came into the timothy sod before it was plowed for corn. Under such conditions it is practically impossible to report true nitrogen availability figures (see plate 1).

TABLE 5
Average percentage of nitrogen recovered by 5-year periods, field experiments 1923-1927

PLOT NUMBER	A. UNLIMED				B. LIMED			
	First 5-year period	Second 5-year period	Third 5-year period	Fourth 5-year period	First 5-year period	Second 5-year period	Third 5-year period*	Fourth 5-year period
5	14.9	14.6	18.7	21.2	13.6	12.8	13.2	9.9
6	14.6	16.2	24.6	11.9	10.9	14.8
8	23.5	16.3	16.3	25.1	37.6	39.1	15.7	32.7
9	43.3	34.0	31.6	40.7	46.3	26.1	20.2	40.8
10	33.4	29.5	29.0	37.3	55.8	35.8	34.8	41.6
11	47.4	28.7	6.3	47.9	40.0	31.9	47.8
12	36.4	25.5	32.4	38.8	43.9	31.5	29.9	37.9
13	30.1	23.4	31.5	32.2	28.8	18.9
14	30.6	29.1	41.4	48.3	24.4	25.6	20.1	28.3
15	21.3	23.7	21.5	19.2	28.7	26.9	15.0	30.9
16	20.7	17.6	19.8	23.1	15.5	14.9
17	Loss	12.9	17.2	11.0	39.2†	86.3†
18	17.8	16.0	18.7	23.1	18.8	15.7	17.6	21.2
20	36.4	24.3	21.3	20.3	32.6	29.3	16.7	24.2
Average...	26.5	22.3	23.6	30.4	30.6	26.0	20.2	31.5

* Average for 4 years. Oats 1919 omitted.

† Omitted from average on account of volunteer clover.

Following the wheat crop of 1925, volunteer clover again appeared on many of the plots on the limed section and this influenced the yields of timothy in 1926 and 1927. Undoubtedly the recoveries for these years would have been higher had it not been for the volunteer clover which came into the check plots to a greater degree than in the nitrogen-treated plots.

Where large amounts of nitrogen are used as in 5A and 5B and 18A and 18B the recoveries are low, which necessarily means that the losses of nitrogen are great.

PERCENTAGE OF NITROGEN AND pH VALUES IN SOIL SAMPLES

Table 6 shows the percentage of nitrogen in samples of soil collected in 1913, 1917, 1922, and 1927, and the pH values for samples collected in 1922 and 1927. In studying the table it should be remembered that certain changes have been made in the fertilizer treatments since the 1922 sampling.

In collecting the samples of soil it has been customary to take the top samples to the depth of about $6\frac{1}{2}$ inches and the subsoil from this depth to 13 inches. The samples were dried and passed through a 2-mm. sieve before being ground for analysis. For the purpose of making comparisons it may be stated that nitrogen determinations made on samples collected from several of these plots in 1909 (one year after the work was started), gave an average of 0.11 per cent nitrogen. A careful study of the table brings out a number of interesting points.

Unlimed section (A plots)

Plots 1 to 4, which have received no nitrogen, show very little change in the nitrogen content. This is due in part to the fact that the crops have been comparatively small, and in part to the fact that the land appears to be a trifle better at this point than in other parts of the field.

Plot 5, which has received 16 tons of manure annually, shows a gradual increase in nitrogen content. The increase from 0.10 per cent in 1913 to 0.135 in 1927 is proof enough that the building-up process is very slow even under favorable conditions.

Plot 6, which also received 16 tons of manure annually up to and including 1922, also shows an increase in the percentage of nitrogen up to 1922. However with the omitting of the manure in 1923 and thereafter, there has been a slight decrease in the percentage of nitrogen as shown by the analysis for 1927. The decrease in yield on this plot has also been referred to.

Plot 7, without any fertilizer, shows a low nitrogen content. This plot has reached a point where it produces practically no crops. The subsoil for this plot also shows a low percentage of nitrogen.

Plot 8, which receives only one-half the standard amount of nitrogen, shows a lower percentage of nitrogen than plots 9, 10, and 11, which received the standard application. Here also the subsoil shows a low percentage of nitrogen.

Plots 9, 10, and 11, which receive nitrate of soda, nitrate of lime, and sulfate of ammonia, respectively, in equivalent amounts, show very little difference in nitrogen content. Plot 12 on the other hand shows a slightly lower percentage than the three preceding plots. The nitrogen for this plot is supplied in the form of calcium cyanamide and it is possible that the calcium, thus supplied, tends to hasten the loss of nitrogen through the formation of calcium nitrate.

Plots 13, 14, 16, 17, and 20 show approximately the same nitrogen content as 9 to 11, while plots 15 and 19 are very much the same as plot 12.

TABLE 6
Total nitrogen and pH values on samples of soil from the unlimed and limed plots

PLOT NUM- BER	FERTILIZER TREATMENT (AS REVISED, 1923-1927)	UNLIMED SECTION (A PLOTS)						LIMED SECTION (B PLOTS)						pH*	
		Nitrogen			pH*			Nitrogen			Soil				
		Soil		Subsoil	Soil		Subsoil	Soil		Subsoil	Soil		Subsoil		
		1913	1917	1922	1927	1922	1927	1913	1917	1922	1927	1922	1927	1927	
		%	%	%	%	%	%	%	%	%	%	%	%	%	
1	Nothing.....	0.1060	0.1030	0.1020	0.0930	0.0680	0.0680	5.4	5.3	5.60	0.0860	0.0770	0.0720	0.0690	0.0510
2	160 pounds muriate of potash.....	0.1100	0.1170	0.1110	0.1030	0.0800	0.0770	5.4	5.2	5.90	0.0870	0.0790	0.0780	0.0750	0.0520
3	320 pounds superphosphate.....	0.1040	0.1140	0.1130	0.1060	0.0720	0.0640	5.4	5.3	5.80	0.0820	0.0750	0.0720	0.0700	0.0490
4	Minerals only.....	0.1180	0.1090	0.1080	0.1000	0.0720	0.0590	5.4	5.4	5.80	0.0860	0.0780	0.0770	0.0780	0.0610
5	Minerals and 16 tons cow manure.....	0.1000	0.1190	0.1340	0.1350	0.0850	0.0840	5.2	5.5	5.60	0.1030	0.1140	0.1280	0.1320	0.0920
6	Minerals only.....	0.0930	0.1230	0.1270	0.1240	0.0970	0.0820	5.1	5.3	5.40	0.1030	0.1190	0.1340	0.1150	0.0860
7	Nothing.....	0.0790	0.0790	0.0740	0.0680	0.0370	0.0420	5.3	4.7	5.40	0.0880	0.0820	0.0800	0.0770	0.0610
8	Minerals and 160 pounds NaNO ₃	0.0880	0.0880	0.0840	0.0820	0.0470	0.0450	5.8	5.5	5.90	0.0800	0.0790	0.0780	0.0780	0.0530
9	Minerals and 320 pounds NaNO ₃	0.0920	0.0980	0.0970	0.0980	0.0640	0.0620	5.8	5.8	6.00	0.0750	0.0810	0.0740	0.0710	0.0520
10	Minerals and Ca(NO ₃) ₂ equivalent to 320 pounds NaNO ₃	0.0940	0.0900	0.0920	0.0900	0.0660	0.0520	5.8	5.7	6.00	0.0810	0.0780	0.0810	0.0780	0.0510
11	Minerals and (NH ₄) ₂ SO ₄ equivalent to 320 pounds NaNO ₃	0.0980	0.0900	0.0950	0.0980	0.0610	0.0520	4.8	4.0	4.80	0.0800	0.0820	0.0780	0.0770	0.0600
12	Minerals and Ca(CN) ₂ equivalent to 320 pounds NaNO ₃	0.0870	0.0840	0.0860	0.0870	0.0480	0.0470	5.8	5.8	5.80	0.0860	0.0900	0.0800	0.0820	0.0560
13	Minerals only.....	0.0930	0.1060	0.1070	0.1010	0.0690	0.0680	5.4	5.1	5.50	0.0810	0.0830	0.0780	0.0750	0.0480
14	Minerals and NaNO ₃ (NH ₄) ₂ SO ₄ (N half and half).....	0.1010	0.1060	0.1080	0.1040	0.0720	0.0630	5.6	5.3	5.50	0.0780	0.0890	0.0810	0.0800	0.0600
15	Minerals and tankage equivalent to 320 pounds NaNO ₃	0.0880	0.0920	0.0870	0.0860	0.0550	0.0500	5.2	5.1	5.10	0.0720	0.0800	0.0750	0.0800	0.0610
16	Minerals only.....	0.0890	0.1010	0.0980	0.0970	0.0640	0.0490	5.2	5.1	5.30	0.0900	0.0900	0.0960	0.0950	0.0660

17	Minerals only.....	0.095	0.098	0.096	0.091	0.059	0.048	5.5	5.2	5.50	0.095	0.100	0.103	0.070	0.055	6.8	6.8
18	Minerals and 16 tons manure and 320 pounds NaNO ₃	0.109	0.117	0.132	0.134	0.074	0.073	6.0	5.9	5.80	0.101	0.119	0.124	0.134	0.065	6.9	7.1
19	Minerals only.....	0.093	0.087	0.091	0.084	0.059	0.052	5.3	5.0	5.20	0.081	0.078	0.082	0.081	0.050	0.046	7.0
20	Minerals and 2 tons rye straw and 320 pounds NaNO ₃	0.096	0.091	0.094	0.098	0.060	0.059	6.0	5.8	5.60	0.083	0.090	0.091	0.092	0.056	0.048	7.0
	Averages.....	0.097	0.101	0.102	0.099	0.065	0.060	5.5	5.3	5.60	0.086	0.098	0.088	0.087	0.060	0.045	6.8
																7.0	
																6.9	

* pH determinations in 1922 by color method; in 1927 by potentiometer.

Plot 18 shows the influence of the manure and nitrate of soda which have been applied, the percentage of nitrogen being practically the same as for plot 5 where manure is used. In both cases the influence of the manure may be observed in the nitrogen content of the subsoil.

The averages for the percentage of nitrogen at the four different sampling periods show a remarkable agreement, indicating practically no change in the nitrogen content of the soil, averages considered, during the last 15 years.

As previously pointed out, certain treatments have brought about rather pronounced changes but when the averages are considered these changes are not apparent.

There is, however, a distinct indication of a slight decrease in the nitrogen content of the subsoil during the past five years. This would seem to make it quite clear that any nitrogen that is leached out of the topsoil is carried on beyond the reach of the plant roots.

With the exception of plot 11 which has become very acid through the continued use of sulfate of ammonia without lime, practically all of these plots show a pH between 5.1 and 6.0, the average in 1922 being 5.5 and in 1927, 5.3. The subsoils taken in 1927 show an average pH of 5.6 which is slightly above the average for the topsoils.

It is of interest to note that where nitrate of soda, nitrate of lime, and calcium cyanamid have been used regularly throughout the entire period (plots 8, 9, 10, 12, 18, and 20) the pH is distinctly above the general average in 1922 and also in 1927. This influence may be traced to the subsoil as may also the influence of the sulfate of ammonia. Aside from these treatments and the ammonium sulfate treatment (plot 11) the fertilizers have apparently had little influence on the soil reaction. In support of this it may be pointed out that plot 3 which has received superphosphate (acid phosphate) annually throughout the period shows the same pH as plot 1 which has received no superphosphate nor any other fertilizer.

Limed section (B plots)

The plots of this section show very much the same variations as those of the unlimed section. For example, plots 5 and 18—continuous treatment with manure—show a gradual increase in nitrogen content and also, after 1913, a higher nitrogen content than the other plots.

Plot 6 which received manure up to and including 1922, shows this increase but, after the manure has been discontinued for five years there is a decided decrease in the percentage of nitrogen.

The average percentages of nitrogen in the soils of the limed section are distinctly lower than the averages for the unlimed section. This is true of both the topsoils and subsoils. The decrease in the subsoils for 1927 is very noticeable.

This greater loss of nitrogen from the limed than from the unlimed section must be explained either on the ground of larger crops removed, or of a greater

loss through leaching. Since the crops grown were non-legumes—corn, oats, wheat, and hay—and therefore were not much increased in yield by the use of lime, it would seem that the loss must be explained on the ground of more rapid nitrification and therefore of a greater loss through leaching.

Reference has already been made to the tendency of volunteer clover to appear on certain of the limed plots and to its entire absence on the unlimed plots. For this reason it would be expected that the limed soils would show a higher percentage of nitrogen than those without lime. The fact that this is not the case gives further proof that the use of lime favors nitrification with the consequent greater loss of nitrates in the drainage waters. It may also be pointed out that lime seems to favor the growth of certain weeds such as the daisy (*Chrysanthemum leucanthemum*), dog fennel (*Anthemis cotula*), and wild carrot (*Daucus carota*). These weeds were abundant in the timothy on the limed plots but noticeably absent on the unlimed section (see plate 2).

It is of interest to note that the 1927 determinations on the soils from the limed plots show a pH value close to 7.0 for all plots. A few of the plots show pH values above 7.0, whereas one, the sulfate of ammonia treated plot, shows a pH value of 6.5. This means that the 2 tons per acre of ground limestone applied in 1923 has kept the soil near the neutral point throughout the five years.

The subsoils for this section have an average pH of 6.9, which is distinctly higher than the average for the subsoils of the unlimed section. It is thus shown that the lime has gradually worked its way down until there is now only a slight difference in the reaction of the topsoil and the subsoil. The subsoils for the nitrate and calcium cyanamid treated plots show a pH a little above the general average as was the case with the topsoils, whereas the sample from the sulfate of ammonia treated plot shows a pH distinctly below the general average.

These determinations throw new light on the lasting qualities of limestone and on its penetration into the subsoil.

SUMMARY

This paper reports the results of the fourth 5-year period (1923–1927) in the nitrogen availability field experiments.

The object of the work has been:

- a. To study the yields of dry matter and nitrogen and the availability of nitrogen under varying nitrogen and lime treatments.
- b. To study the influence of the lime and nitrogen treatment on the percentage of nitrogen in the dry matter.
- c. To study the availability of the nitrogen, in several nitrogenous materials, in a soil deficient in lime and also in one well supplied with lime.
- d. To study the influence of large amounts of organic matter in the form of manure, on crop yields and on the utilization of nitrate nitrogen.
- e. To study the changes in the nitrogen content of the soil under different nitrogen treatments and also with and without lime.

Note is made of certain changes in the plan beginning with 1923.

With a few exceptions the lime treatment did not give pronounced increases in yield, the average increase being 2779 pounds of total dry matter for the 5 years or about 556 pounds annually. However, in this connection it must be remembered that the rotation included no legumes.

With the exception of plot 11A (unlimed, and ammonium sulfate as a source of nitrogen) the nitrogen treatment increased the yields over the check plots.

For both sections the mineral nitrogenous materials gave greater increases than did organic nitrogen (tankage).

On the limed section the increase with sulfate of ammonia was slightly greater than with nitrate of soda, but less than with nitrate of lime. On the unlimed section the yield on the sulfate of ammonia plot was reduced to a very low amount.

The greatest increase was with a combination of nitrate of soda and manure. This increase for the 5-year period was 20,229 pounds, or slightly more than 4,000 pounds per year. This increase, however, was obtained with a great loss of nitrogen.

Where the nitrogenous fertilizer has been discontinued for a period of 5 years, there are still increases in yield over the check plots, but these increases are generally less than the increases at the close of the third 5-year period.

With a few exceptions the percentage of nitrogen in the dry matter has not been greatly influenced by the nitrogen treatments. Generally speaking, where the nitrogen treatment has been heavy, the percentage of nitrogen in the dry matter has been increased. This is particularly true of the plots that have received heavy applications of manure or manure and nitrate of soda.

The average percentage of nitrogen for all treatments, for a given crop on the limed section, does not differ very much from the average for the corresponding crop on the unlimed section.

The yields of total nitrogen follow rather closely the yields of dry matter.

The percentage of nitrogen recovered is irregular, because of a number of factors. The average recoveries for the limed section are in most cases only a little above those for the unlimed section.

The 5-year averages show a recovery of 30.44 per cent for the unlimed section and 31.53 per cent for the limed section. These figures are somewhat higher than the averages for the first, second, and third 5-year periods.

Attention is called to the fact that where lime, phosphate, and potash have been used freely, with a limited supply of available nitrogen, volunteer clover comes in with grain and hay although none has been seeded. This has very materially affected the results on some of the nitrogen-starved plots.

With the exception of those plots that receive rather extreme treatment the percentage of nitrogen in the soil has not changed much since 1913. The average percentage of nitrogen in soils from the unlimed section is about 0.10 per cent and from the limed section about 0.088 per cent. Those plots that have received heavy applications of manure and manure with nitrate of soda have gradually gained in nitrogen content.

The loss of nitrogen is greater from the lime treated plots than from those without lime.

The average pH value for the unlimed soils was 5.3 in 1922 and 5.5 in 1927. For the limed soils it was 6.8 in 1922 and 7.0 in 1927.

Where nitrate of soda, nitrate of lime, and calcium cyanamid have been used the pH value is higher than the general average. Where sulfate of ammonia has been used with lime the pH is below the general average for the limed section.

This work gives emphasis to the following points:

- a. The great difficulty in maintaining the nitrogen supply of the soil when non-legume crops only are grown.
- b. The small percentage of the applied nitrogen that is recovered in the crop under field conditions, and therefore the great loss of nitrogen from soils that are constantly under cultivation.
- c. The imperative need of lime in connection with fertilizers that are physiologically acid.
- d. The effect of lime in depleting the nitrogen supply of the soil when no legume crops are grown, and the slight gain in yield of general farm crops under this condition.
- e. The ease with which clover may be grown if the conditions are made favorable by the use of lime, phosphate, and potash.
- f. The superiority of mineral nitrogenous materials over the organic forms.

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PLATE I

FIG. 1. Plot 4B (left) lime and minerals, but no nitrogen applied 1908-1923; volunteer clover following grain and hay explains the excellent crop of corn; yield 46.4 bushels per acre.

Plot 5B (right) lime minerals, and 16 tons manure annually 1908-1923; yield 42.5 bushels per acre.

FIG. 2. Plot 19B (right) lime and minerals, but no nitrogen 1908 to 1923; volunteer clover following grain and hay explains the excellent crop of corn; yield 43 bushels per acre.

Plot 20B (left) lime, minerals, and nitrate of soda (320 pounds per acre), and rye straw 1908 to 1923; yield 37.7 bushels per acre.



FIG. 1



FIG. 2

PLATE 2

FIG. 1. Plots 1A-4A (4A next to white line), without lime since 1908. Note absence of daisies in timothy. Note also the presence of daisies in the timothy on the limed plots, in the background to left.

FIG. 2. Plot 4B. Timothy showing abundant growth of daisies, where lime has been applied to keep the soil at about pH 6.9 to 7.1.

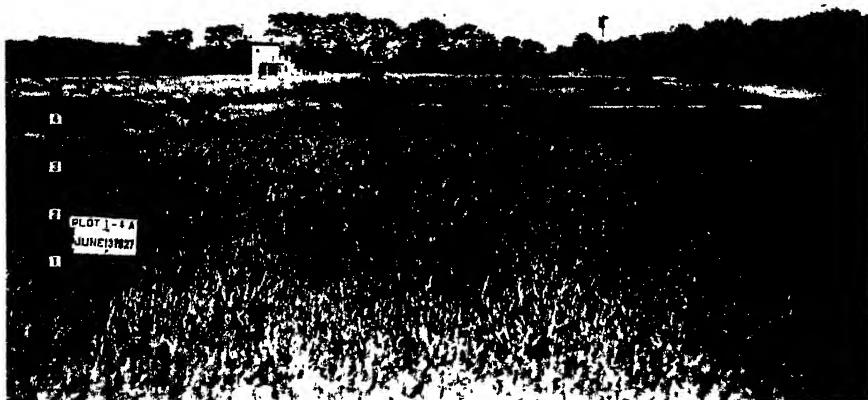


FIG. 1



FIG. 2

A "DEFICIENCY DISEASE": THE LACK OF AVAILABLE MANGANESE IN A LIME-INDUCED CHLOROSIS¹

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The purpose of this paper is to call attention to some of the results which have been obtained during the past three years in the correction of a "chlorosis," or as it is sometimes called, a "yellowing," as noted on crops growing on soils that have been neutralized at the Rhode Island Agricultural Experiment Station. Very small applications of manganese compounds have alleviated the malady, and the occurrence of chlorosis has been found to be associated with a very low manganese content of the affected plants as compared with that of normal plants on similar but more acid soils (1).

The work of McHargue (2) and others has demonstrated the requirements of plants for manganese when grown in solution and sand cultures from which the manganese had been very carefully eliminated. Inhibited growth was accompanied by yellowing of leaves and finally the development of dead areas. These phenomena correspond to those noted with the chlorotic plants growing on near-neutral soils on the Rhode Island station plats. The near-neutral condition of these soils has resulted from liming over a period of years.

Recently, Zimmerly (5) has reported similar observations with chlorotic spinach at the Virginia Truck Experiment Station. This spinach was grown on soils of lower acidity than pH 6.5.

Skinner and Reed (4) have advanced the theory that manganese benefits plants indirectly by increasing the oxidative power of the soil. This hardly seems to be the whole story, since McLean (3) has shown that similar beneficial results may be obtained directly by injecting chlorotic leaves with manganous sulfate solution. This points to the beneficial action being localized within the plant.

THE 1925 EXPERIMENTS

Whatever may be the mechanism of the manganese relation, the fact remains that with chlorotic plants growing on near-neutral soils, small applications of manganese salts used in the form of a spray or mixed with chemical fertilizers serve to cure and prevent chlorosis and thereby materially to influence yields.

The results of the 1925 experiments have been reported elsewhere (1). In

¹ Contribution No. 364 of the station.

brief, chlorosis had been noted for some time previous to that year and efforts made unsuccessfully to correct the condition by use of iron salts. In 1925, a spray solution containing 8 pounds per acre of manganous sulfate was used to correct chlorosis in spinach and oats. That very small amounts of manganese are necessary for normal plant metabolism is evident from the small amounts (60 p.p.m.) found in healthy plants growing on more acid-soil conditions and from the small amount of this element removed by a spinach crop (0.1 pound per acre). The 1925 application of manganese increased yields of spinach from 20 to 215 per cent. An increase of 67 per cent was noted between samples of oats taken from treated and untreated areas.

TABLE 1
Yields per acre of 1926 crops on Project I

CROP	MANGANESE TREATMENT	PLAT 74	PLAT 76	PLAT 78	PLAT 80	PLAT 82
Lettuce.....	Mn	cwt.	cwt.	cwt.	cwt.	cwt.
	No Mn	267.0	289.0	287.25	234.75	28.5
Beans.....	Mn	bushels	bushels	bushels	bushels	bushels
	No Mn	2.3	1.8	4.8	6.5	2.0
Corn grain.....	Mn	103.0	139.0	113.0	97.0	89.0
	No Mn	56.0	113.0	75.0	47.0	73.0
Onions.....	Mn	501.0	717.0	471.0	573.0	3.0
	No Mn	39.0	222.0	60.0	78.0	3.0
Corn stover.....	Mn	tons	tons	tons	tons	tons
	No Mn	2.80	4.58	4.95	4.73	3.95
Mangels.....	Mn	28.58	34.65	37.95	30.83	4.20
	No Mn	18.90	29.40	19.58	30.23	1.05

THE 1926 EXPERIMENTS

In 1926, the area previously used for "Project I" was employed for experimental work on chlorosis. This area consists of 5 plats, 4 of which had been heavily limed with different neutralizing materials, and had a range of pH 7 to 8, while the fifth, plat 82, had received no lime and had an acidity of approximately pH 4.7. This area received a uniform fertilization. An initial application of 30 pounds per acre of manganous sulfate mixed with the chemical fertilizer was made to one-fourth of each plat. The whole area was planted to miscellaneous crops, consisting of lettuce, corn, beans, onions, and mangels. These were planted in rows running the length of each plat in such a way that

portions of each crop were grown on both manganeseed and non-manganeseed areas. An additional application was made of 15 pounds per acre of manganeseous sulfate in solution.

In table 1 are given the yields of these crops as harvested from comparable areas showing the increase due to manganese treatment. It will be noted that corn, lettuce, onions, and mangels responded to the manganese application markedly, whereas beans were not so definitely benefited. In addition to yield differences, benefit in color of leaves was noted with millet.

TABLE 2
Dry weights of hay varieties in 5 square yard strips of plat 74S

STRIP	MANGANESE TREATMENT	ALFALFA	CLOVER	OATS	MISCELLANEOUS	TOTAL
		gm.	gm.	gm.	gm.	gm.
No. 1	Mn	220.0	278.0	1,475.0	275.8	2,248.8
	No Mn	59.6	350.5	65.0	436.5	911.6
No. 2	Mn	174.2	236.2	1,385.0	229.1	2,024.5
	No Mn	87.3	286.2	41.0	284.5	699.0
No. 3	Mn	121.0	230.3	975.0	387.8	1,714.1
	No Mn	121.2	229.0	230.0	525.0	1,105.2

THE 1927 EXPERIMENTS

In 1927, the same area (Project I) was seeded down with the following mixture:

	pounds per acre
Alfalfa.	. 5
Alsike.....	2
Biennial sweet clover.....	3
Medium red clover.....	3
Oats.....	16
Orchard grass.....	2
Redtop.....	3
Timothy.....	2

A uniform fertilizer and also 30 pounds of manganeseous sulfate in the chemical fertilizer were applied to the same quarter of each plat. The acidity was approximately the same as in the previous year. On July 16, 1927, measured strips of the hay crop were cut in such a way that each strip included a definite portion of the manganeseed and non-manganeseed areas. The various plant species were carefully separated and each sample was air-dried. In table 2, the air-dry weights of these varieties are given.

It will be seen that a very consistent benefit was obtained with manganese in the case of oats and alfalfa, whereas the sweet clovers and miscellaneous plants

(including redtop, timothy, orchard grass, and weeds) do not show, under competitive conditions, such a consistent story. This yield difference agreed with visual observations made upon the color of the leaves of the various kinds of plants.

As a result of the experience gained during 1925 and 1926, the plats devoted to the growing of market garden crops were given in 1927 a uniform application of 30 pounds per acre of manganous sulfate mixed with the chemical fertilizers. In order to obtain a measure of the benefit from this application, to certain half plats no application of manganese was made. With beets the chlorotic condition manifests itself at first as an abnormal redness of the leaves. This is followed by the appearance of dead areas. The redness appears to be due to the lessening in amount of the green chlorophyll pigment thus allowing the anthocyanins to predominate. As fall beets did not seem to respond to the initial manganese applied in the fertilizer mixture, two additional applications of 10 and 20 pounds per acre of manganous sulfate were made in the form of a

TABLE 3
Increases in yields per acre of market garden crops due to manganese treatment, 1927

CROP	PLAT	MANGANESE TREATMENT	YIELD	INCREASE
			bushels	per cent
Spinach (spring).....	96W $\frac{1}{2}$	Mn	2,435	0.4
	96E $\frac{1}{2}$	No Mn	2,425	
Spinach (fall).....	89E $\frac{1}{2}$	Mn	1,565	133.0
	89W $\frac{1}{2}$	No Mn	670	
Beets (fall).....	86E $\frac{1}{2}$	Mn	332	137.0
	86W $\frac{1}{2}$	No Mn	89	

spray. In the case of fall spinach, manganese was also applied in solution. The greater yield differences as shown in table 3 indicate that the solution method is the better way to apply the manganese salt.

DISCUSSION

Increasing interest is being shown in the chemical elements that are found in minute quantities in plant tissue. Gradually evidence is being accumulated to show that under certain conditions insufficient amounts of zinc, boron, manganese, etc., may be the cause of subnormal growth. Definite phenomena are often found which serve to indicate the need for such deficient elements. The chlorosis of crop plants growing on neutralized soils furnishes an excellent example of such a phenomenon and is associated with a lack of available manganese for normal growth. Such a chlorosis may well be termed a "deficiency disease" and is a definite pathological condition. It is suggested that a specific example of this phenomenon may be spinach "yellows."

From the results of experiments extending over a 3-year period on the Rhode Island experimental plats there seems to be conclusive evidence to show that through heavy liming soil conditions may be created in which many plants develop chlorosis. This phenomenon and the accompanying decrease in yields may be prevented and remedied by applications of small amounts of a manganous sulfate, either incorporated with the chemical fertilizer application or applied in the form of a spray to the growing plants. There is also some evidence to indicate that with some crops the spray method is the more efficacious.

SUMMARY

The correction of the "deficiency disease" resulting from the lack of available manganese in a lime-induced chlorosis is discussed and experimental data from the Rhode Island experimental plats are given.

1. Attention is briefly drawn to the recent literature dealing with this subject.
2. Reference is made to the 1925 experiments. The application of 8 pounds per acre of manganous sulfate corrected the chlorotic condition of spinach and increased the yield 215 per cent.
3. The 1926 and 1927 experiments are discussed in detail. Absence of chlorosis and increased yields were noted with tilled crops of corn, lettuce, onions, and mangels when manganous sulfate was applied. Hay varieties in competition also benefited greatly, as is shown by counts made on equal strips through the treated and untreated areas.
4. Evidence is given to show that better results are obtained when the manganous salt is applied in solution.

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THE DRAINAGE OF LAND OVERLYING ARTESIAN BASINS¹

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PART I.—THE MOVEMENT OF WATER INTO DRAINS

The heterogeneous nature of the subsoils of our agricultural valleys is such as to defy attempts to predict *with precision* what will happen with respect to the movement of the water which they contain in any given case. An engineer may design a drainage system that will produce satisfactory results, but he learns to proceed with caution when dealing with problems involving important hidden factors which he cannot hope to determine *completely*. The analysis here presented will apply rigorously only to the ideal cases treated, and the degree to which it may apply to the actual drainage problem will depend upon the similarity between the idealized description of the problem and the problem itself.

This article has been written with the Cache-Valley area (Utah) foremost in mind. This valley is structural in origin, and under its lower-lying areas the fill consists of more than 1000 feet of incoherent debris, the fine-textured soils and subsoils to a depth of 50 feet or more having been deposited from the waters of the prehistoric Lake Bonneville. Below this surface stratum the water in the gravel is under hydrostatic pressure, and artesian wells are abundant over the entire district. During the summer when evaporation is high the surface crust in most places is kept comparatively dry. When cool, cloudy weather comes and the rate of evaporation diminishes, the thin surface stratum in many places becomes completely saturated.

In order to force water vertically upward through the resisting silt and clay the excess pressure in the water-bearing gravel will be utilized so that the pressure excess measured at various points upward from the gravel will show a gradual decrease, but during times of wet and stormy weather there may be considerable residual pressure at the depths at which drains are customarily placed.

Three important ideal cases will be considered:

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Case I. The water moving radially into horizontal drain tile, the soil uniform for a great depth.

The total flow Q for a given length l of the drain converging through any given equipotential semi-cylindrical surface of radius r will satisfy the following equation:

$$Q = \rho f \pi r l v \quad (A)$$

where v represents the velocity of flow toward the drain, ρ the density of the water, and f a fraction introduced for the purpose of reducing the total surface of the semi-cylinder to net surface unobstructed by the presence of soil particles.

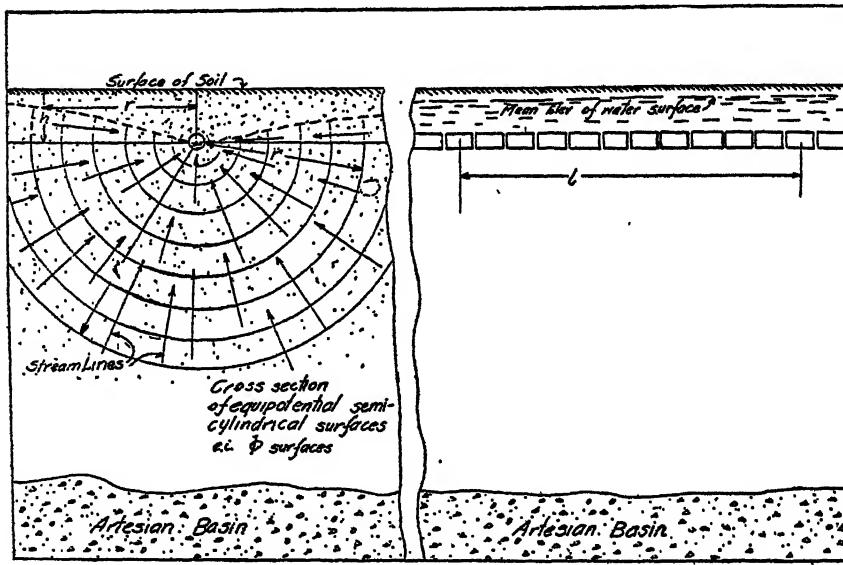


FIG. 1. TYPICAL DIAGRAM ILLUSTRATING THE MOVEMENT OF WATER INTO HORIZONTAL DRAIN TILE PLACED IN FINE-TEXTURED SOIL OF GREAT DEPTH OVER-LYING AN ARTESIAN BASIN—CASE I

Darcy's law expresses the fact that for velocities which are not too great the velocity is proportional to the pressure head lost, which, for this case, may be stated algebraically,

$$v = (k/f)d\Phi/dr \quad (B)^3$$

where Φ is the so-called potential function, or, to use the language of the engineer with an appropriate choice of units, the elevation of the hydraulic gradient

³ In order to avoid the use of the factor f it has been thought advisable to split Darcy's constant K into two factors: $K = (1/f)k$. By this expedient, f will disappear from equation (C). The constant k will be designated the transmission constant. This will be a characteristic constant for each soil.

above a horizontal datum plane. Where the movement takes place in a horizontal plane the ratio of the hydrostatic pressure p to the density of the water ρ may be substituted in place of Φ . It is clear, however, that even though the velocity is everywhere zero, the hydrostatic pressure will vary vertically so that the resultant pressure force is just balanced by the force of gravity and the substitution of Φ for p/ρ automatically takes care of the correction for elevation.

The elimination of v from equations (A) and (B) gives the differential equation,

$$Q = \pi l \rho r k (d\Phi/dr) \quad (C)$$

Integrating this between the limits Φ_2 and Φ_1 and r_2 and r_1 we obtain the desired equation,

$$\Phi_2 - \Phi_1 = \frac{Q}{\rho \pi l k} \ln \frac{r_2}{r_1} \quad (D)^*$$

If the application of equation (D) is now restricted to the horizontal plane containing the tile and if all pressures are measured with atmospheric pressure as the zero base, the ratio of this hydrostatic pressure p to the density ρ may be substituted for the potential function Φ , and the equation becomes

$$p_2 - p_1 = \frac{Q}{\pi l k} \ln \frac{r_2}{r_1} = C \ln \frac{r_2}{r_1} \quad (E)$$

where,

$$C = \frac{Q}{\pi l k} \quad (a)$$

If we regard r_1 as the radius of the tile, p_1 of equation (E) will reduce to atmospheric pressure (or to zero according to the convention given) and a general expression for the pressure p at any distance r from the drain in a horizontal plane with two independent constants, C and r_1 , may therefore be obtained, but which may be written for convenience so as to involve Q and k explicitly,

$$p = \frac{Q}{\pi l k} \ln \frac{r}{r_1} \quad (F)$$

If the condition be imposed that the pressure p be just sufficient to bring the water to the surface of the ground in a standpipe installed with good contact with the soil at the level of the drain and at the distance r from the drain, p may be replaced by the factor ρgh , where h is the depth of the drain and g the gravity field constant, giving a final equation,

$$Q = \frac{\pi \rho l k g h}{\ln \frac{r}{r_1}} \quad (G)$$

* The symbol \ln standing for the natural logarithm.

Case II. Perforated pipe placed vertically in a soil uniform to a great depth, the pressure in the well being reduced to zero by pumping at a point at depth h below the surface of the ground.

In this case all but a negligible part of the water will be assumed to flow radially toward the vertical "tile" or well of radius r_1 through vertical cylind-

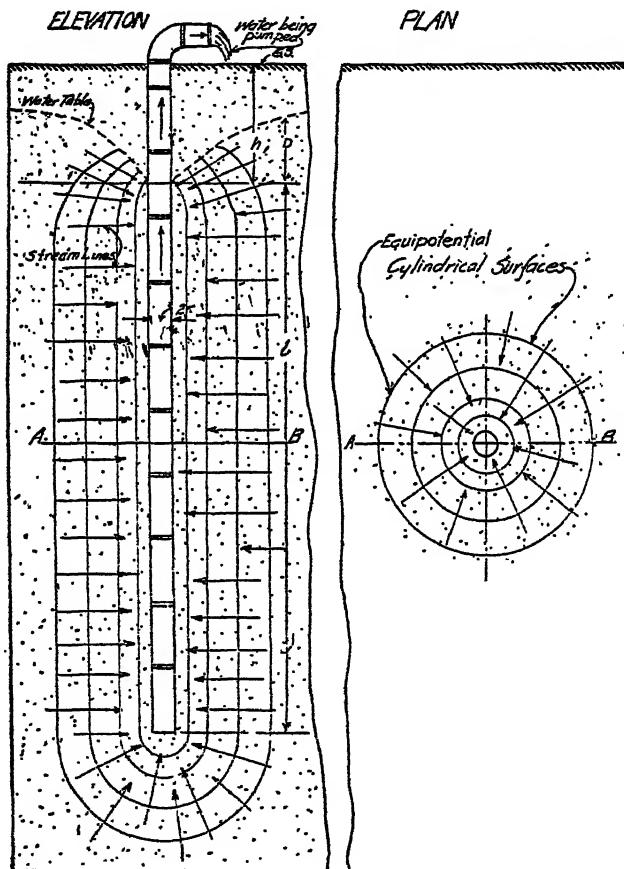


FIG. 2. TYPICAL DIAGRAM ILLUSTRATING THE MOVEMENT OF WATER INTO A VERTICAL PUMP DRAIN PLACED IN SOIL OF COMPARATIVE UNIFORM TEXTURE TO A GREAT DEPTH—CASE II

drical equipotential surfaces of variable radius r rather than through horizontal semi-cylindrical equipotential surfaces. This will necessitate the introduction of a factor 2 in equation (G), giving,

$$\frac{2 \pi \rho l kgh}{\ln \frac{r}{r_1}} \quad (G_1)$$

In this case l refers to the length of the well segment in the water-bearing material whose transmission constant is k and is assumed to be large in comparison with the quantity h . Horizontal planes will cut the equipotential surfaces in circles rather than in straight lines as in case I.

Case III. The well is driven just into the gravel, which extends downward to great depths; the pressure is reduced to zero at some depth h below the

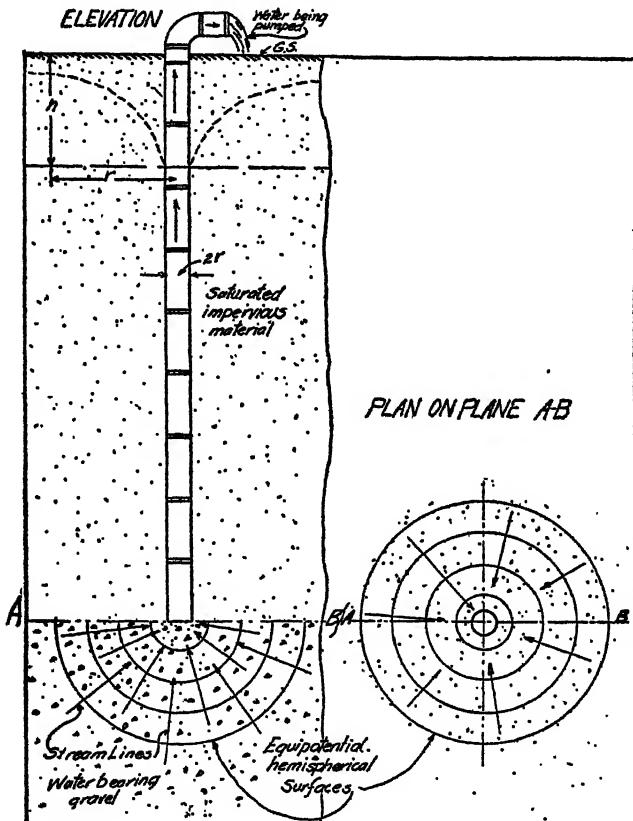


FIG. 3. TYPICAL DIAGRAM ILLUSTRATING THE MOVEMENT OF WATER INTO A VERTICAL PUMP DRAIN FROM WATER-BEARING ARTESIAN STRATUM; THE DRAIN PENETRATING THE IMPERVIOUS MATERIAL AND OPENING INTO THE WATER-BEARING STRATUM—CASE III

ground surface by pumping; and the water converges toward the bottom of the well through hemispherical equipotential surfaces with center at the well. This differs from case II only in the fact that the water converges from great depths toward a center just beneath the overlying clay stratum rather than toward the axis of the well.

For this case, equation (A) is modified to read,

$$Q = 2\rho f \pi^2 r \quad (\text{Aa})$$

equation (C) to read,

$$Q = 2\pi r^2 k (d\Phi/dr) \quad (\text{Ca})$$

and equation (E) for a horizontal plane at the depth h below the ground surface,

$$p_2 - p_1 = \frac{Q}{2 \pi k} \left(\frac{1}{r_1} - \frac{1}{r_2} \right) \quad (\text{Ea})$$

If we regard r_1 as the radius of the hemispherical "intake" of the well cavity with the pressure p_1 at this point equal to some constant magnitude determined by the magnitude of h , and if we neglect the friction loss due to vertical flow through the clay equation (Ea) for the horizontal plane at depth h becomes,

$$p = \frac{Q}{2 \pi k} \left(\frac{1}{r_1} - \frac{1}{r} \right) \quad (\text{Fa})$$

and then again making the pressure p just sufficient to allow the water in a standpipe in contact with the soil at the level of the water in the well to come to the surface of the ground, we obtain,

$$Q = \frac{2 \pi k \rho g r_1 r h}{r - r_1}. \quad (\text{Ga})$$

Where r_1 is negligible in comparison with r , this equation reduces to,

$$Q = 2\pi k \rho g r_1 h \quad (\text{Ha})$$

which gives the discharge of a single well.

In order to reclaim the land it is presumed that each well should remove the water as fast as it enters the soil under a given surface area and in addition maintain the water table below the zone of root action. On the assumption that k does not vary with the depth it would appear from comparison of equations (G) and (G₁) that the water may be removed with half as much tile if placed in a vertical position. After providing for a sufficient amount of drainage to remove all the water at the rate at which it enters, it remains to determine the magnitudes h in such a way as to maintain the water table at a safe distance below the surface of the ground.

A serious economic question may arise when the installation of drains horizontally and vertically is considered. The vertical drain will involve the expense of pumping the water through a distance h from a series of wells, whereas it may flow away by gravity with the other system.⁵

⁵ It is to be noted that the quantity of water available is proportional to the depth h in all three cases considered and also to the length of the drain in the first two cases, if r is independent of h and l , and k a constant. If the r 's, h 's, and l 's are the same in cases I and

The surface stratum of clay in the Cache Valley area is very compact and does not permit the water to pass readily through it, being fairly uniform throughout the entire 50 feet. The pressure in the gravel is sufficient to support a column of water of about 75 feet (i.e., 25 feet above the surface of the ground). In order to obtain an approximate idea of the required spacing of drains on the basis of case I, we may equate the right-hand member of equation (G) to the right-hand member of equation (M) of part II of this paper. First making the substitutions,

$$A = 2lr \quad (b)$$

$$p' = \rho g L \quad (c)$$

and after simplification, the following relation is thus obtained,

$$\frac{(L - w)}{w} 2r \ln \frac{r}{r_1} = \pi h \quad (K)^*$$

By substituting in this equation the values, $L = 75$ feet, $w = 50$ feet, $h = 8$ feet, $r_1 = 1$ foot, we obtain approximately 21 feet for the value of $2r$, representing the required distance between drains in order that the pressure may not exceed ρgh at any point in the horizontal plane containing the tile. Substituting $h = 16$ feet we obtain approximately 35 feet for the required drain spacing.

The wells of case III will extend into the gravel, and the ratio of the k 's for gravel and clay will be of the order of 40,000 to 1 so that a very decided advantage will accrue in the matter of the yield from each well. If perforated casing is introduced through the gravel, equation (G₁) will hold for the flow from the gravel, but if the well barely opens into the gravel, equation (G_a) would no doubt apply, provided the gravel were of considerable depth. It is clear in

II, the yield will be double in the second case, but the ratio R of the areas reclaimed, case I to case II, would be,

$$R = \frac{2lr}{\pi r^2} = \frac{2l}{\pi r} \quad (I)$$

The existing pressure distribution and the character of the soil, however, will determine the magnitudes of the Q 's in either case after h , r_1 , and l are arbitrarily chosen.

In the case of horizontal drains the total excavation will vary as the product hls in case I, where l represents the length of the tile considered and s the width of the drain, whereas the total excavation in case II will vary as the sum of h and $l/2$ and as the square of the width s of drain or diameter of well, the factor 1/2 arising from the fact that only half as much tile is required when placed in a vertical position, the ratio R , of the amount of excavation, case I to case II being,

$$R_s = \frac{\pi}{4} \left(h + \frac{l}{2} \right) s^2 \quad \frac{4}{\pi \left(\frac{s}{l} + \frac{s}{2h} \right)} \quad (J)$$

* It should be noted that the constant h has disappeared from equation (K) by cancellation and that this relation is therefore independent of the character of the soil.

this case, if it is assumed as a first approximation that r is independent of h , or if r_1 is small compared with r , that Q is proportional to the product hr_1 . The size of the well, i.e., the radius r_1 of the "spherical" well cavity, therefore, will also have an important influence on the performance of the well.⁷

The cost of lifting the water through the height h may be sufficient to make the vertical drains undesirable in any case, but where the water so pumped becomes available as a source of supply for irrigation the value of the water may be sufficient to justify the expense of pumping and under such conditions the question remains as to the magnitudes h and r_1 of equation (Ga). As stated, Q will increase with h and r_1 , and the number of wells required after these factors have been adjusted economically will depend upon the total of inflow Q_1 of water into the soil. Increasing h with r_1 fixed, or increasing r_1 with h fixed, will increase the value of Q until the upper limit Q_1 is reached, and this will increase the pressure gradient in the horizontal plane, giving a steeper slope to the $p-r$ curve, so that, from the standpoint of uniformity alone, it would be desirable to make h and r_1 small with small yield from each well and with numerous wells. However, from the standpoint of overhead expense in pumping, this extreme would not be satisfactory, and the problem, therefore, will resolve itself into determining the magnitudes h and r_1 which will give minimum expense for excavation, installation of drains, pumping and distribution of water pumped, subject to the condition that the pressure at the depth h shall not exceed ρgh for any value of r . In addition, provision should be made by means of a safety factor to lower the water-table below this point in order to provide a healthy root zone for the crops to be produced.

In view of what has been said above, it will perhaps be admitted that certain theoretical advantages favor the installation of vertical systems even though the factor k remains unchanged with increasing depth, i.e., with silt or clay extending to great depths. Practical engineers, of course, recognize a very great advantage if a stratum is found for which k has a large value; this would no doubt constitute the primary motive in the selection of the vertical system. In case III the movement of water through the clay overlying the gravel has been neglected in comparison with that through the gravel. Preliminary determinations in the physics laboratory give values of k for clay, Greenville loam, and fine sand, were c.g.s. units have been chosen of 1×10^{-9} , 6×10^{-8} , and 4×10^{-5} , respectively, which are in the ratio of 1 to 60 to 40,000.

PART II.—COST ELEMENTS IN DRAINAGE BY PUMPING

The following analysis is presented as suggestive and preliminary, looking toward a method of determining the economical depth from which the water

⁷ It should be noted that equations (G), (G₁), and (Ga) are homogeneous in Q and k , and therefore the ratio of Q to k only is involved. Inasmuch as these magnitudes are proportional, for given boundary conditions, i.e., for given values of h , r_1 , and the pressure at the remote boundary, the form of the $p-r$ function is independent of the character of the soil, although the water available is proportional to the magnitude of k .

should be pumped and the diameter of drainage wells. Provisional figures are given for costs of drainage.

Let the cost of drainage of the entire tract by means of pumping from wells be represented by E . This will contain an overhead for each well, including pump, casing, etc., which will be represented by E_o , cost for excavation, E_e , and capital cost for power, E_p . If n represents the number of wells, the following equation may be written:

$$E = n(E_o + E_e + E_p) \quad (\text{A})$$

where n satisfies the condition,

$$nQ = Q_1 \quad (\text{B})$$

The capital cost per unit quantity of water pumped, z , will be given by the equation,

$$z = E/Q_1 = \frac{E_o + E_e + E_p}{Q} \quad (\text{C})$$

Eliminating Q from the equation (Ga) of part I and equation (C) above, the following equation may be obtained:

$$z = \frac{(E_o + E_e + E_p)(r - r_1)}{2\pi k \rho g r_1 h} \quad (\text{D})$$

If the magnitude, e , is defined as the cost per unit of energy expended in excavation, which is taken as a constant, the following equation may be written:

$$E_e = \pi r_1^2 \rho' e g \int_0^w x dx = \frac{\pi}{2} \rho' e g r_1^2 w^2 \quad (\text{E})$$

where x measures the distance from the surface of the ground to the point from which the earth is removed, w the total depth of the well, and ρ' the density of the soil removed.

The quantity P may also be defined as the capital cost per unit of power used from year to year for pumping, satisfying the equation,

$$E_p = Phg \quad (\text{F})$$

If the condition is introduced that r_1 is to be negligible in comparison with r , which means that the pressure at the h level will be reduced to ρgh at a considerable distance from the well, from obvious substitutions, the following will be obtained:

$$z = \frac{E_o}{2\pi k \rho g r_1 h} + \frac{\pi er_1 w^2 g \rho'}{2(2\pi k \rho g h)} + (1/F) Phg \quad (\text{G})$$

where F represents the efficiency of the pumping plant.

Expressing the condition for minimum value of z ,

$$dz = \frac{\partial z}{\partial r_1} dr_1 + \frac{\partial z}{\partial h} dh = 0 \quad (\text{H})$$

from which, since r_1 and h are independent, the following is obtained

$$\frac{-E_o}{2\pi k \rho g r_1^2 h} + \frac{\pi e w^2 g \rho'}{2(2\pi k \rho g h^2)} = 0 \quad (I)$$

and

$$\frac{-E_o}{2\pi k \rho g r_1 h^2} - \frac{e \pi r_1 w^2 g \rho'}{2(2\pi k \rho g h^2)} + \frac{P_g}{F} = 0 \quad (J)$$

Solving these two equations (I) and (J) for r_1 and h ,

$$r_1 = \sqrt{\frac{2 E_o}{e \pi w^2 g \rho'}} \quad (K)$$

$$h = \left\{ \frac{w F}{\rho g K P} \sqrt{\frac{E_o e \rho'}{2 \pi g}} \right\}^{\frac{1}{2}} \quad (L)$$

By substituting values obtained from equations (K) and (L) back into equation (Ha) of part I, the flow from each well will be obtained. If the magnitude Q_1 for the given known area to be reclaimed were known it would be possible by means of equation (B) of part II, to determine the number n of such wells and the area to be reclaimed by each. This will imply also, of course, a knowledge of the various constants appearing in equations (K) and (L).

As a first approximation, it may be assumed that the entire quantity Q_1 evaporates from the surface after passing through the stratum of clay, and Darcy's equation may be written as an explicit function of the pressure p' at the boundary between gravel and clay, the depth w of the well, the transmission constant for the clay k_c , the area involved A , and the density of the water ρ ,

$$Q = \frac{p' - \rho gw}{w} k_c A \quad (M)$$

The value obtained above for a single well may then be substituted for Q in (M) and the equation solved for A , the area reclaimed by a single well.

No attempt has been made to determine with precision the constants involved in this equation. In order, however, to illustrate the case and to obtain results that may be regarded as approximate, the following values have been chosen:

$$E_o = \$800$$

$$e = 4 \times 10^{-12} \text{ dollars per erg, or } 5.42 \times 10^{-5} \text{ dollars per foot-pound}$$

$$P = 2.9 \times 10^{-7} \text{ dollars per erg per second, or } \$2900 \text{ per kilowatt}$$

$$w = 1525 \text{ cm., or 50 feet}$$

$$k = 4 \times 10^{-6} \text{ c.g.s. units}$$

$$k_c = 1 \times 10^{-9} \text{ c.g.s. units}$$

$$F = 0.5$$

$$p' = 2.25 \times 10^6 \text{ dynes per square centimeter or 75 feet of water}$$

$$\rho' = 2.75 \text{ gm. per cubic centimeter}$$

$$g = 980 \text{ c.g.s. units}$$

Inasmuch as the soil is compact and saturated with moisture, the density has been taken as 2.75 as a safe upper limit. In order to obtain approximation for the energy cost unit e ,⁸ the supposition was made that a man should earn approximately \$4 for excavating a well 8 feet in diameter and 3 feet deep. The value chosen for P will give 6 per cent interest on investment for power at 2 cents per kilowatt-hour.

By substituting these values in equations (K) and (L) and reducing the results to feet as the units of length, 9.38 feet is obtained for the most economical diameter of the well and 9.28 feet for the most economical height of lift h . Taking $k = 4 \times 10^{-6}$ for gravel and substituting these values again in equation (Ha) and reducing units to gallons per minute, 170 gallons per minute is obtained for the yield from each well. Substituting this value, after an appropriate reduction of units, in formula (M), together with the field values, which are tentative, $p'/\rho - w = 25$ feet of water, $w = 50$ feet, $k_c = 1 \times 10^{-9}$ c.g.s., and after again changing units, a value of 500 acres for the quantity A is obtained.

A series of wells one for each half section of land, each well yielding 170 gallons per minute, diameter 9 feet, depth 50 feet (to the gravel), with a lift of 9 feet (with a safety factor of about $1\frac{1}{2}$), would appear to produce most efficient results. It is presumed that the pumps will be operated continuously or that excessive quantities of water will be pumped during the summer. Additional pumps must be installed to take care of water already flowing from sloughs and springs not accounted for in the calculations from equation (M). It is apparent also that several feet should be added to the depth h to assure healthy conditions in the zone of root action.

If equation (M) is divided through by the area A , the amount of water moving upward through the clay per unit area per unit time will be obtained. The z of equation (G) represents the cost per unit quantity per unit time. The product $z(Q/A)$, therefore, will represent the cost per unit area E_u . Expressing this in terms of z and the fundamental magnitudes determining Q ,

$$\begin{aligned} E_u &= \frac{z(Lg\rho - wg\rho)k_c}{w} \\ &= \frac{z(L - w)gk_c\rho}{w} \end{aligned} \quad (N)$$

where L represents the length of the column of water that would be supported by a pressure p' , k_c being the transmission constant for the clay.

⁸ It may be noted that r_1 varies directly as the square root of E_u , inversely as the square root of e , so that an error of 100 per cent in either of these magnitudes will result in about a 41 per cent error in r_1 . The quantity h varies directly as the product of the fourth root of E_u and e and, therefore, an error of 100 per cent in either of these magnitudes will result in an error of about 19 per cent in h . The depth h varies inversely as the square root of P so that an error of 100 per cent in this quantity will result in an error of about 41 per cent in h .

If the values chosen above for the constants are in the neighborhood of the correct values, the values obtained for r_1 and h , for maximum efficiency, will be approximately correct. As will be noted from equation (G), z is a linear function of these economic magnitudes, and computations for z and also E_u

TABLE 1

Cost per unit quantity of water expressed in dollars per gallon per minute, for different values of radius of well and height of lift

HEIGHT OF LIFT <i>feet</i>	RADIUS OF WELL									
	1 foot	2 feet	3 feet	4 feet	5 feet	6 feet	7 feet	8 feet	9 feet	10 feet
5	\$51.60	\$31.50	\$26.20	\$24.50	\$24.30	\$24.90	\$25.80	\$27.10	\$28.50	\$30.00
10	33.95	23.90	21.30	20.45	20.30	20.60	21.10	21.70	22.40	23.20
15	31.70	25.10	23.30	22.70	22.60	22.80	23.14	23.60	24.00	24.50
20	33.40	28.40	27.00	26.60	26.30	26.70	26.90	27.20	27.60	28.00
25	36.50	32.50	31.40	31.20	31.20	31.20	31.30	31.60	31.80	32.10
30	40.40	37.00	36.20	35.90	35.90	36.00	36.10	36.30	36.50	36.90
35	44.80	41.90	41.20	40.90	40.90	41.00	41.10	41.30	41.50	41.80
40	49.40	46.90	46.30	46.00	46.00	46.10	46.20	46.40	46.60	46.80
45	54.20	52.00	51.50	51.20	51.10	51.20	51.50	51.60	51.70	51.80
50	59.20	57.20	56.60	56.50	56.50	56.60	56.70	56.90	57.10	57.10

TABLE 2

Cost per unit of area reclaimed, expressed in dollars per acre

HEIGHT OF LIFT <i>(h)</i>	RADIUS OF WELL									
	1 foot	2 feet	3 feet	4 feet	5 feet	6 feet	7 feet	8 feet	9 feet	10 feet
5	\$16.26	\$9.95	\$8.26	\$7.74	\$7.68	\$7.85	\$8.15	\$8.54	\$8.98	\$9.46
10	10.71	7.55	6.71	6.45	6.42	6.51	6.66	6.85	7.07	7.31
15	10.01	7.90	7.34	7.16	7.14	7.20	7.30	7.43	7.57	7.73
20	10.52	8.94	8.52	8.39	8.37	8.41	8.49	8.58	8.70	8.82
25	11.51	10.24	9.91	9.80	9.79	9.83	9.89	9.97	10.02	10.15
30	12.75	11.69	11.41	11.33	11.32	11.35	11.39	11.45	11.53	11.61
35	14.12	13.22	12.98	12.90	12.90	12.92	12.96	13.01	13.08	13.15
40	15.58	14.80	14.58	14.51	14.51	14.53	14.57	14.61	14.67	14.73
45	17.10	16.40	16.21	16.15	16.15	16.17	16.19	16.24	16.29	16.34
50	18.65	18.02	17.86	17.80	17.80	17.81	17.84	17.88	17.93	17.98

with various values assigned to the constants involved may be made without difficulty. In tables 1 and 2 calculations are presented for z and E_u for a considerable range in values of r_1 and h with the values of the constants as given above. It is to be noted from table 2 that for the ideal r_1 and h the cost is in the neighborhood of \$6.50 per acre, the greatest cost over the range con-

sidered being \$18.65 per acre for a well of 1 foot radius and the height of h equal to 50 feet.

As a matter of convenience for reference, tables 3 and 4 are given, table 3 showing the influence of the variation of the magnitudes E_o and E_e on the value

TABLE 3

"Efficient" radius of well in feet for varying overhead costs (E_o) and for varying costs per unit of energy expended in excavation (e)

COST PER UNIT OF ENERGY IN EXCAVATION IN DOLLARS PER ERG (e)	OVERHEAD COST OF EACH WELL IN DOLLARS (E_o)									
	\$100	\$200	\$300	\$400	\$500	\$600	\$700	\$800	\$900	\$1000
1×10^{-12}	3.29	4.67	5.72	6.60	7.39	8.09	8.74	9.33	9.90	10.4
2×10^{-12}	2.34	3.29	4.05	4.67	5.22	5.72	6.18	6.60	7.00	7.39
3×10^{-12}	1.91	2.70	3.29	3.81	4.26	4.67	5.04	5.39	5.72	6.02
4×10^{-12}	1.64	2.34	2.86	3.29	3.69	4.04	4.36	4.67	4.95	5.22
5×10^{-12}	1.46	2.10	2.56	2.95	3.29	3.62	3.90	4.17	4.42	4.67
6×10^{-12}	1.35	1.91	2.34	2.70	3.01	3.29	3.56	3.81	4.04	4.26
7×10^{-12}	1.24	1.76	2.16	2.50	2.79	3.06	3.29	3.52	3.74	3.93
8×10^{-12}	1.18	1.64	2.02	2.34	2.60	2.86	3.09	3.29	3.50	3.69
9×10^{-12}	1.09	1.55	1.91	2.20	2.46	2.70	2.91	3.11	3.29	3.48
10×10^{-12}	1.04	1.46	1.80	2.10	2.34	2.56	2.77	2.95	3.13	3.29

TABLE 4

"Efficient" height of lift, expressed in feet, for varying character of soil, k , expressed in c.g.s. units with a factor 10^{-5} omitted, and varying power costs, P , expressed in dollars per erg per second

POWER COSTS (P) IN DOLLARS PER ERG PER SECOND	TRANSMISSION CONSTANT $\times 10^5$									
	$k = 1$	$k = 2$	$k = 3$	$k = 4$	$k = 5$	$k = 6$	$k = 7$	$k = 8$	$k = 9$	$k = 10$
1×10^{-7}	31.6	22.3	18.2	15.8	14.1	12.9	12.0	11.2	10.5	10.0
2×10^{-7}	22.3	15.8	12.9	11.2	10.0	9.2	8.5	7.9	7.5	7.1
3×10^{-7}	18.2	12.9	10.5	9.2	8.1	7.5	6.9	6.5	6.1	5.8
4×10^{-7}	15.8	11.2	9.2	7.9	7.1	6.5	6.0	5.6	5.3	5.0
5×10^{-7}	14.1	10.0	8.1	7.1	6.3	5.8	5.4	5.0	4.7	4.5
6×10^{-7}	12.9	9.2	7.5	6.5	5.8	5.3	4.9	4.6	4.3	4.1
7×10^{-7}	12.0	8.5	6.9	6.0	5.4	4.9	4.5	4.2	4.0	3.7
8×10^{-7}	11.2	7.9	6.5	5.6	5.0	4.6	4.2	4.0	3.7	3.6
9×10^{-7}	10.5	7.5	6.1	5.3	4.7	4.3	4.0	3.7	3.5	3.3
10×10^{-7}	10.0	7.1	5.8	5.0	4.5	4.1	3.7	3.6	3.3	3.1

of the "efficient" r_1 , and table 4 showing the influence of k and E_p upon the "efficient" h . As has been noted previously, the value of h varies as the fourth root of the product of E_o and E_e and, therefore, will not be materially influenced by small changes in these quantities.

COLLOIDAL BEHAVIOR OF SOILS AND SOIL FERTILITY: IV. ANION EFFECT ON THE PRECIPITATION REACTIONS AND DEGREE OF DISPERSION OF ALUMINUM AND IRON HYDROXIDES

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The toxicity of iron and aluminum to plants is a well-known phenomenon. It is generally agreed that aluminum as well as iron toxicity is determined by the degree of dispersion. The plants absorb the aluminum and iron in the molecular state; the cells of the plant act as a semipermeable membrane. On the basis of the researches of Czapec and others, Comber (1) suggests that a highly dispersed sol may be used by plants. It thus becomes important to know the factors governing the degree of dispersion of aluminum and iron in the system soil-soil solution. Reaction alone does not determine the degree of dispersion, as will be shown. The anions, because of their absorption or because of some other force, influence the state in which iron or aluminum exists more perhaps than does the reaction.

The reaction limits at which aluminum ceases to be toxic, according to Magistad¹ (4), are in terms of pH 5.0. Magistad did not, however, determine the reaction limits at which aluminum changes from the crystalline state to the sol and finally the gel. Neither did he evaluate the influence of the anions on the precipitation reaction of aluminum. Line (3) also tried to determine the reaction limits at which aluminum is toxic. He went a step further than Magistad inasmuch as he investigated the effect of phosphates on the elimination of aluminum from a true solution. He showed that with phosphates in solution all of the aluminum precipitates at pH 3.4. He did not, however, consider the various other inorganic anions that usually are found in the soil. Neither did he attempt to determine the state of aggregation as influenced by the reaction and the anions.

Miller (5) considered the solubility of aluminum as influenced by anions from the standpoint of water purification. He did not, however, determine the transition stages of the various states of aggregation. From the standpoint of aluminum toxicity to plants the conditions of state are the important phase to be considered.

¹ For a more complete review of the aluminum problem see Joffe and McLean (2).

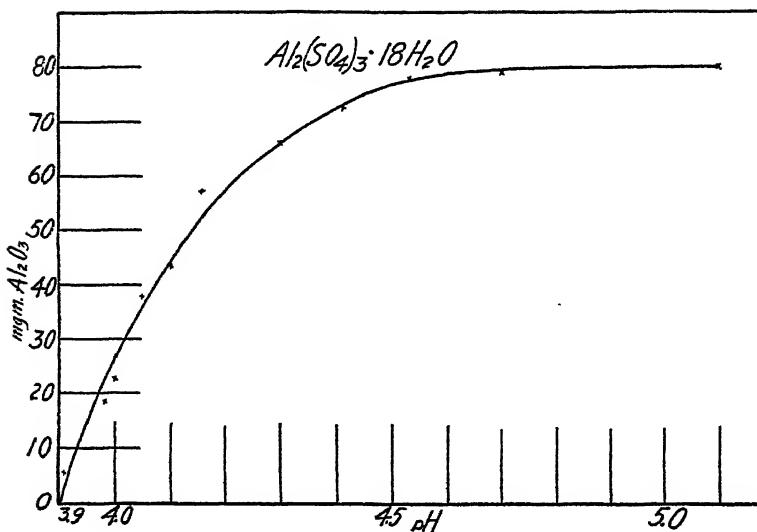
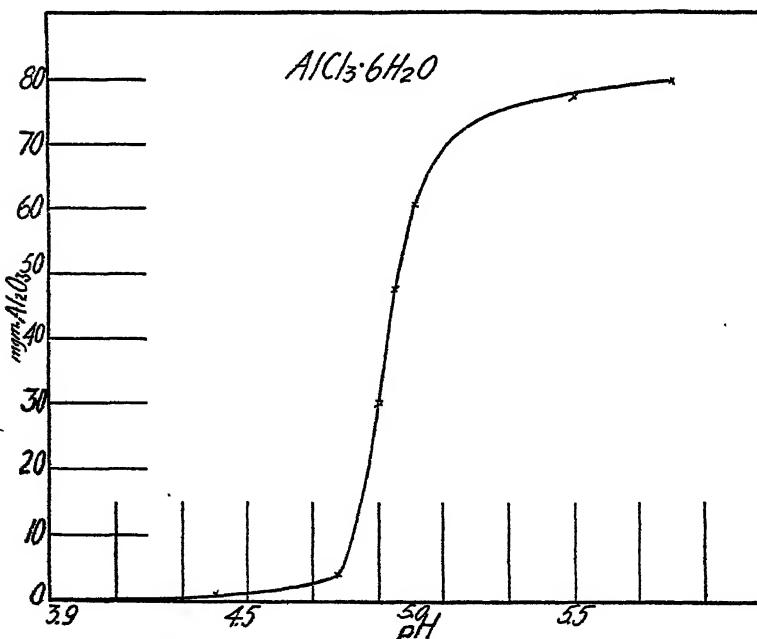
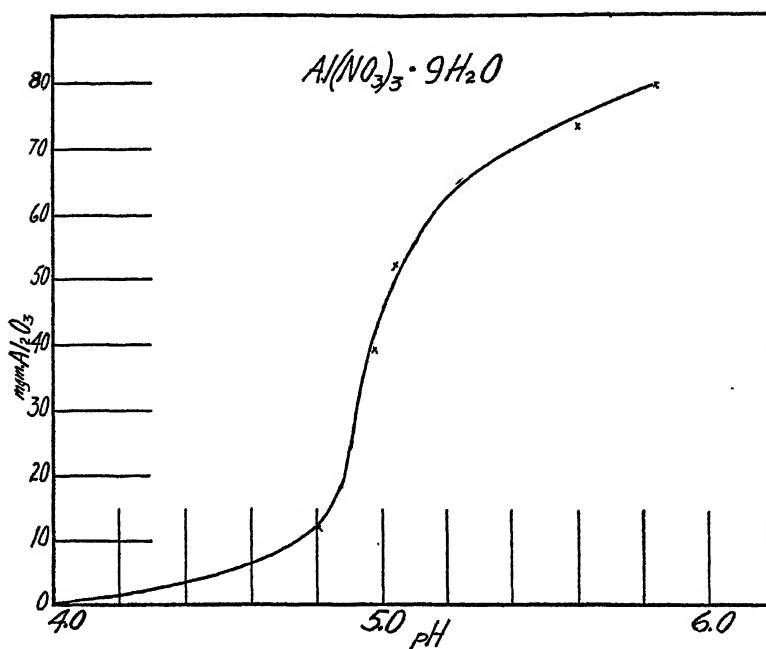
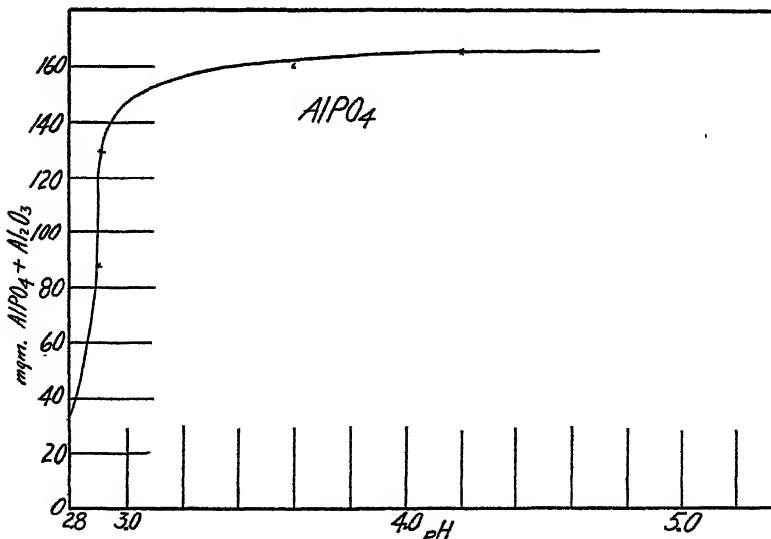
FIG. 1. ALUMINUM GEL FORMATION CURVE IN THE PRESENCE OF SO₄ ANIONS

FIG. 2. ALUMINUM GEL FORMATION CURVE IN THE PRESENCE OF Cl ANIONS

FIG. 3. ALUMINUM GEL FORMATION CURVE IN THE PRESENCE OF NO_3^- ANIONSFIG. 4. ALUMINUM GEL FORMATION CURVE IN THE PRESENCE OF PO_4^{3-} ANIONS

CONDITIONS INFLUENCING STATE OF AGGREGATION OF Al

Experimental. The experiments with aluminum have been reported in detail elsewhere (2) and will be discussed here only briefly.

Figure 1 gives the zone of H-ion concentration at which aluminum is precipitated in the presence of the SO_4^{2-} anion. Already at pH 4.0 about 25 per cent of the Al is in the gel state. At pH 4.7 to 4.8 all of the aluminum has been precipitated.

Dialysis experiments in collodion bags on the various filtrates from the $\text{Al}_2(\text{SO}_4)_3$ precipitates at different H-ion concentrations showed that the aluminum which remained in solution was dialyzable. Thus, under the conditions of the experiment, no sol state was formed in the presence of the SO_4^{2-} anion.

Figure 2 gives the curve of the aluminum hydroxide gel found in the presence of the Cl anion. It will be noted that the gel formation begins at pH 4.8. At pH 5.1 almost 90 per cent of the aluminum was precipitated, and at pH 5.8 complete precipitation took place. Thus the range of reaction at which gel formation is possible, in the presence of Cl anions, is very narrow. Data obtained on the dialyzable aluminum showed that the molecularly dispersed aluminum in the presence of the Cl anion persists almost up to the point of complete precipitation. There was, however, a definite sol state, as evidenced by the amount of aluminum remaining in the dialyzing bag. The behavior of the aluminum in the presence of the Cl ion, from the standpoint of its toxicity in soil, is important inasmuch as normal soils contain but few Cl ions; and besides most normal soils rarely become so acid as to give a pH reading of 5.1.

Figure 3 gives the curve of the precipitation reactions of aluminum as the gel in the presence of the NO_3^- ion. In general the curve is similar to that of the Cl ion curve; there is a slight shift towards the alkaline side in respect of complete precipitation of the aluminum. Only at pH 5.8 to 6.0 is all of the aluminum precipitated. In soils where the nitrifying processes are very active there is a possibility of some of the Al going into the molecular state provided no other bivalent anions are present in solution.

Figure 4 gives the curve of aluminum gel found in the presence of the PO_4^{3-} anion. It will be noted that at pH 3.1 to 3.2 practically all of the aluminum has been precipitated. At pH 3.8 to 4.0 no Al could be detected in the filtrate. Thus in the presence of soluble phosphates no Al is possible in solution under normal soil conditions. With no excess of phosphate in solution the precipitate is not pure AlPO_4 but a mixture of AlPO_4 and $\text{Al}(\text{OH})_3$. For a discussion of this point the reader is referred to the paper mentioned above (2).

CONDITIONS INFLUENCING STATE OF AGGREGATION OF Fe

Experimental. From the respective salts [FeCl_3 , $\text{Fe}(\text{NO}_3)_3$, and $\text{Fe}_2(\text{SO}_4)_3$] of iron 2 \times 0.0075 M solutions of Fe_2O_3 were prepared, and 50 cc. placed in a

100 cc.-volumetric flask. Variable amounts of 0.1 *N* KOH were added in order to establish a range of reaction points, as expressed by the pH readings, and the solution was finally made up to 100 cc. Such a solution was equivalent to 0.0075 *M* Fe_2O_3 . After the solution had stood 24 hours the amount of gel formed was determined either directly by filtration or indirectly by determining the Fe_2O_3 in an aliquot of the supernatant solution. The filtrate, or an entire duplicate solution, was placed in collodion bags and dialyzed in distilled water, the water being changed every 24 hours until no iron appeared in the dialyzate. The iron dialyzed was considered as being in the molecular state of aggregation; the iron that remained in the bag minus the amount of gel previously determined was figured as the sol. In this manner the co-existing states of aggregation were separated.

TABLE I
The states of aggregation in an iron colloidal solution, 0.0075 M Fe_2O_3 , in the presence of the SO_4 anion

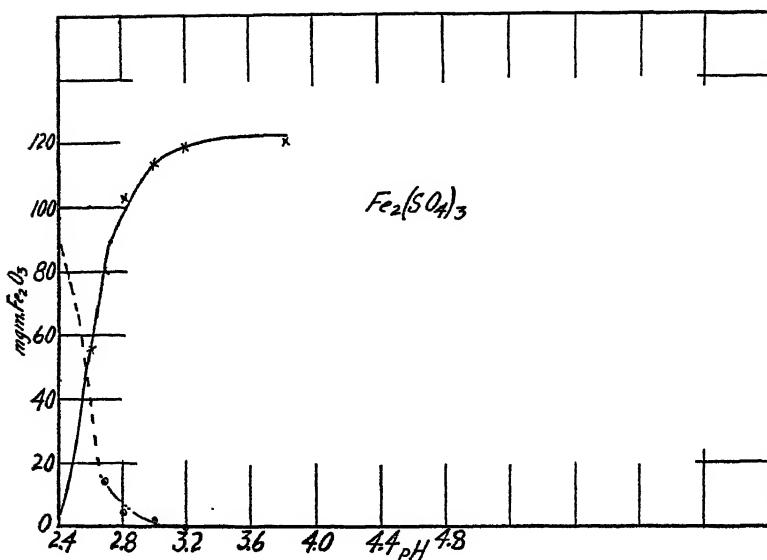
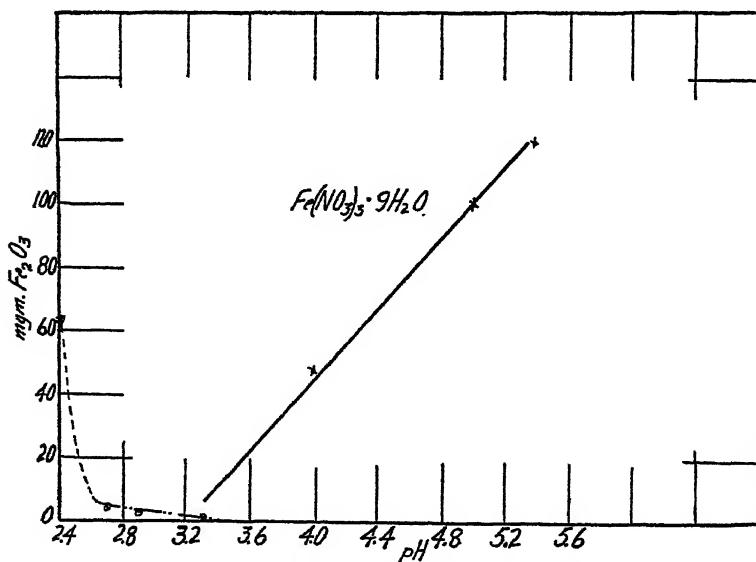
LABORATORY NUMBER	0.1 <i>N</i> KOH ADDED TO 50 CC. OF $2 \times 0.0075 \text{ M}$ Fe_2O_3 SOLUTION AS $\text{Fe}_2(\text{SO}_4)_3$	REACTION OF SOLUTION	Fe_2O_3 AS GEL	Fe_2O_3 AS SOL	Fe_2O_3 IN MOLECULAR STATE
	cc.	pH	mgm.	mgm.	mgm.
1	0.0	2.2	0.0	23.0	98.6
2	32.5	2.7	80.0	26.8	14.8
3	35.0	2.8	103.4	12.8	5.4
4	37.5	2.8	106.4	11.0	4.2
5	40.0	3.0	114.0	3.5	4.1
6	42.5	3.2	118.6	1.6	1.4
7	43.5	3.8	121.0	0.0	0.0
8	45.0	5.6	121.6	0.0	0.0

EFFECT OF SO_4 ANION ON TRANSITION STATE OF Fe COLLOIDS

Table 1 gives the plan and the results of the experiments. Figure 5 gives the curve showing the zone of H-ion concentration at which iron precipitates from a 0.0075 *M* solution of Fe_2O_3 as $\text{Fe}_2(\text{SO}_4)_3$, and the curve of the dialyzable iron at the various reaction points in the presence of the SO_4 anion.

It is interesting to note that at pH 3.8 (more accurately between 3.2 and 3.8) all of the iron exists in the gel state. Such a degree of acidity rarely, if ever, exists in normal soils. Naturally this precludes the iron from being a toxic factor whenever the SO_4 anion is present. On the other hand it indicates that if it were possible to imagine a soil condition with SO_4 anions as found in the pure solution study, there would be a complete locking up of the iron, and iron starvation would be the consequence.

The curve representing the amount of iron dialyzed is divided into two parts: the dash part represents the amount of Fe dialyzed when no KOH or water was added to the 100 cc. of 0.0075 *M* solution of $\text{Fe}_2(\text{SO}_4)_3$; the dash

FIG. 5. IRON GEL AND DIALYZING CURVES IN THE PRESENCE OF SO_4 ANIONSFIG. 6. IRON GEL AND DIALYZING CURVES IN THE PRESENCE OF NO_3 ANIONS

and dotted line part gives the amount of Fe dialyzed as the reaction of the dispersion medium changes. It may be seen that at this particular concentration hydrolytic effects influence the state of aggregation, inasmuch as close to 20 per cent of the Fe is converted into the sol, which upon dialysis is converted into gel.

EFFECT OF NO_3^- ANION ON THE TRANSITION STATES OF Fe COLLOIDS

Table 2 gives the plan and the results of the experiments. Figure 6 gives the curve showing the zone of H-ion concentration at which iron precipitates from a 0.0075 M solution of Fe_2O_3 , and the curve of dialyzable iron at the various reaction points in the presence of the NO_3^- anion.

The outstanding feature of the precipitation curve is that the various points of gel formation fall almost in a straight line, showing that in the

TABLE 2

The states of aggregation in an iron colloidal solution, 0.0075 M Fe_2O_3 in the presence of the NO_3^- anion

LABORATORY NUMBER	0.1 N KOH ADDED TO 50 CC. $2 \times 0.0075 \text{ M}$ Fe_2O_3 SOLUTION AS $\text{Fe}(\text{NO}_3)_3$	REACTION OF SOLUTION	Fe_2O_3 AS GEL	Fe_2O_3 AS SOL	Fe_2O_3 IN MOLECULAR STATE
	cc.	pH	mgm.	mgm.	mgm.
1	0.0		0.0	55.8	63.8
2	33.0	2.7	0.0	115.1	4.5
3	34.0	2.9	0.0	116.8	2.8
4	35.0	3.3	0.0	118.0	1.6
5	36.0	4.0	48.2	71.4	0.0
6	37.0	5.0	99.6	20.0	0.0
7	37.5	5.4	119.6	0.0	0.0
8	38.0	6.2	119.6	0.0	0.0

presence of the NO_3^- anion the absolute rate of increase in gel formation is constant. The curve also shows that at pH 5.4 all of the iron is precipitated. In the humid regions soils with a reaction of pH 5.4 and even lower are encountered. There is no danger, however, of Fe being in solution in the presence of the NO_3^- anion until pH 3.3 has been reached, as may be seen from table 2 and the dialysis curve. Small amounts of molecularly dispersed Fe appear only at this reaction point (pH 3.3), but such a reaction is out of the range of normal soils.

The portion of the dialysis curve (dash line) indicating the condition of the state of aggregation of a pure 0.0075 M $\text{Fe}(\text{NO}_3)_3$ solution shows that more than 50 per cent of the Fe exists in the molecular state and a little less than 50 per cent in the sol state. It is to be remembered that the ratio of the two states is true for this concentration of Fe only. The electrolytic effects and hence the conditions of state of aggregation change with the concentration, a well-known phenomenon in colloid chemistry.

It may also be mentioned that with the removal of the molecularly dispersed Fe, the sol state within the dialyzing sac does not go into the gel as is the case with the SO_4 anion. The differential adsorption of the SO_4 and NO_3 anions and the difference in the amount of electrical charge on them will explain this behavior. Several months elapsed before any of the sol was transformed into gel.

At this point it will be interesting to analyze the data in table 2 on the sol state of the Fe colloid in the presence of the NO_3 anion. Even at pH 5.0 about 16 per cent of the iron is in the sol state. If the theory of Comber (1) on the absorption of colloidally dispersed substances by plants is true, there

TABLE 3
The state of aggregation in an iron colloidal solution, 0.0075 M Fe_2O_3 in the presence of the Cl anion

LABORATORY NUMBER	0.1 N KOH ADDED TO 50 CC. $2 \times 0.0075 \text{ M}$ Fe_2O_3 SOLUTION AS FeCl_3	REACTION OF SOLUTION	Fe_2O_3 AS GEL	Fe_2O_3 AS SOL	Fe_2O_3 IN MOLECULAR STATE
	cc.	pH	mgm.	mgm.	mgm.
1	0.0		0.0	51.0	68.6
2	20.0	2.4	0.0	84.7	34.9
3	25.0	2.4	0.0	95.5	24.1
4	28.0	2.6	0.0	95.5	24.1
5	35.0	3.8	0.0	107.5	12.1
6	36.0	4.0	0.0	109.3	10.3
7	36.5	4.0	0.0	109.8	9.8
8	37.0	4.2	0.0	110.7	8.9
9	38.0	4.3	0.0	111.6	8.0
10	39.0	4.4	0.0	111.6	8.0
11	40.0	4.6	0.0	116.6	3.0
12	40.2	4.6	0.0	119.0	Trace
13	40.4	4.6	0.0	119.0	Trace
14	40.6	4.8	19.3	100.3	0.0
15	40.8	4.8	34.9	84.7	0.0
16	41.0	5.0	57.2	62.4	0.0
17	41.1	5.5	119.6	0.0	0.0

is the possibility of Fe in the presence of the NO_3 anions being absorbed at pH 5.0. It is to be remembered, however, that the change of state of any chemical substance is in reality a change in state of aggregation. The closer we get to the gel state the greater is the aggregation. In other words, the size of the particles increases as we approach the gel state. The sol which exists at pH 5.0 approaches conditions in the disperse medium inducive to coagulation and must therefore be of a lower degree of dispersion than the sols at lower pH values. It is logical to assume that the larger the size of the particles the more difficult it is to explain the absorption of them by plants.

With the NO_3 anion the zone of possible colloid absorption (high degree of

dispersion—transition stage from sol to molecular state) lies in the range of reactions which do not support plant life and which are not found in normal soils.

EFFECT OF Cl ANION ON THE TRANSITION STATES OF Fe COLLOIDS

Table 3 gives the plan and the results of the experiments. Figure 7 gives the curve showing the zone of H-ion concentration at which iron precipitates from a 0.0075 M solution of Fe_2O_3 in the presence of the Cl anion, and the curve of dialyzable iron at the various H-ion concentrations imparted to the solutions by adding different amounts of KOH, or without any additions—dash part of the curve, representing a 0.0075 M solution of Fe_2O_3 as FeCl_3 .

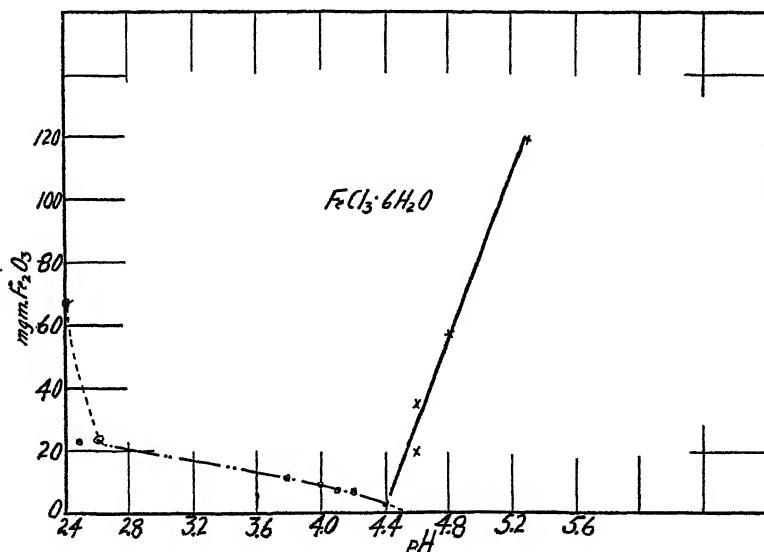


FIG. 7. IRON GEL AND DIALYZING CURVES IN THE PRESENCE OF Cl ANIONS

As with the NO_3^- anion the precipitation curve is a straight line. In this respect the valency effects are similar. The zone of H-ion concentration at which precipitation takes place is slightly different when the effects of the two anions are compared; with the Cl anion, precipitation is slightly delayed. The complete precipitation reaction is, however, almost identical.

The portion of the dialysis curve showing the condition of the state of aggregation of a pure 0.0075 M FeCl_3 solution shows that more than 50 per cent (57.4) of the Fe exists in the molecular state, the rest being in the sol state. Again the Cl anion behaved in a similar manner as the NO_3^- anion.

EFFECT OF A MIXTURE OF ANIONS ON THE TRANSITION STATES OF Fe COLLOIDS

Table 4 gives the plan and the results of the experiments. Figure 8 gives the curve showing the zone of H-ion concentration at which iron precipitates,

and the curve of dialyzable iron at the various H-ion concentrations in the presence of a mixture of SO_4^- , NO_3^- , and Cl^- anions.

It will be noted that the curve of gel formation is primarily influenced by the SO_4^- anion. It may almost be superimposed on the curve of the gel formation

TABLE 4

The state of aggregation in an iron colloidal solution, 0.0075 M Fe_2O_3 in the presence of a mixture of SO_4^- , NO_3^- , and Cl^- anions

LABORATORY NUMBER	0.1 N KOH ADDED TO 50 CC. 2×0.0075 M Fe_2O_3 SOLUTION AS FeCl_3 , $\text{Fe}(\text{NO}_3)_3$, AND $\text{Fe}_2(\text{SO}_4)_3$	REACTION OF SOLUTION	Fe_2O_3 AS GEL	Fe_2O_3 AS SOL	Fe_2O_3 IN MOLECULAR STATE
	cc.	pH	mgm.	mgm.	mgm.
1	0.0		0.0	73.1	46.5
2	10.0	2.3	70.5	30.0	19.1
3	15.0	2.4	79.6	28.0	12.0
4	20.0	2.6	103.0	11.2	5.4
5	25.0	2.8	113.4	6.0	Trace
6	30.0	4.7	119.6	0.0	0.0

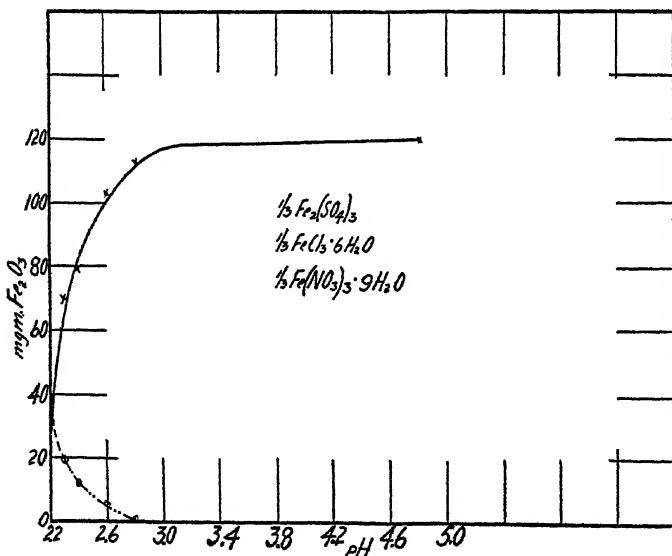


FIG. 8. IRON GEL AND DIALYZING CURVES IN THE PRESENCE OF A MIXTURE OF SO_4^- , NO_3^- , AND Cl^- ANIONS

in the presence of the SO_4^- anion alone (fig. 5). This is important, inasmuch as it shows that the SO_4^- anion, which is almost always present in the soil solution, dominates the precipitation reactions of iron.

The curve representing the amount of iron dialyzed shows that the molecular state of aggregation of iron has decreased as compared with the data of the SO_4 anion alone. On the other hand, the amount of sol has increased surpassing even the solutions with either NO_3 or Cl anion alone. This indicates the effect of the Cl and NO_3 anions: they seem to favor the formation of the sol, or, more accurately stated, their coagulation power, due to the amount of electrical charge carried by them, is lower.

It is interesting to record that the sol has been transformed into the gel upon dialysis even in the solution where no KOH has been added. Apparently this is due to the adsorbed SO_4 anion, since, although no test for Cl could be detected in the solution within the collodion sac, there were noticeable traces of the SO_4 anion.

DISCUSSION

The data presented clearly show that the solubility of aluminum and iron and the formation of the different states of aggregation are controlled not only by the H-ion concentration but primarily by the anion present. No data have been presented on the effect of the phosphate anion on the precipitation of Fe since the iron phosphates are formed at a very high H-ion concentration, which is never encountered in soils.

Al is completely precipitated, or gel is formed, at pH 4.7 whenever the SO_4 anion is present. The introduction of soluble phosphates shifts the point of gel formation to pH 4.2. With Cl and NO_3 anions the complete transformation of the Al into the gel takes place only at pH 5.7 to 6.0, a range frequently met with in soils. It is therefore possible that under soil conditions where intensive nitrifying activity goes on there may be some aluminum existing in a state of high degree of dispersion, even as far as molecular dispersion. However, since almost all soils invariably contain some SO_4 and PO_4 anions the completion of gel formation is shifted toward the points on the pH scale characteristic for the complete precipitation of the Al in the presence of the SO_4 or PO_4 anions.

From the studies reported it is logical to assume that no aluminum in true solution may exist in the soil if the stoichiometric reactions considered prevail in the soil. That this is not entirely true might be expected from the complexity of factors existing in the colloid system—soil-soil solution—where the phases of the system are interchangeable, that is, the soil colloids are at times the disperse means and the soil solution becomes the disperse phase. Ordinarily the reverse is true, but such a condition in time of drought is possible. Of course this will influence the relationships of the transition states of the Al; this point will be discussed in a subsequent paper of this series dealing with the movement of Al and Fe in the soil. At this point will be worth mentioning the possibility of Al in solution due to the dissociation of the existing electrolytic colloids—the Al-silicate complex—in which the Al may be ionized to some extent.

The differential precipitation effects of various anions on iron colloids has been studied by Duclaux, as quoted by Zsigmondy (6). With the SO_4^- anion it takes 17×10^{-6} gm. equivalents to coagulate 10 cc. of a hydrosol having 0.0203 gm. atoms of Fe in a liter; with the citrate anion— 16.5×10^{-6} ; with CO_3^- — 17×10^{-6} ; with PO_4^- — 19×10^{-6} ; with OH^- — 16.1×10^{-6} ; and with NO_3^- — 1880×10^{-6} . In the studies reported, the effects of three anions on the states of aggregation of Fe have been established for the condition of the experiments. Similar effects might be expected in the soil. The existence of free iron in molecular state is almost precluded for all normal soils even in the presence of the monovalent anions. The mixture of the anions, which is most likely to exist in the soil, behaves almost like the SO_4^- anion by itself.

The following question suggests itself: If the inorganic anions suppress the solubility of the iron, where do the plants obtain the iron for their metabolic activities? The answer to this must be sought in the solubility effects of the organic acids and other organic substances which serve as solvents for iron. The organic solvents are of a transitory nature, being completely mineralized by the microbial activity. In all probability these are responsible for the iron supply in the soil solution.

In considering the source of supply of iron for plant use, one must not forget the effects of CO_2 on the reaction of the soil in the vicinity of the roots; one must also remember the acidity produced at points of active nitrification. These are known as the effects of local action.

SUMMARY

1. In the presence of the SO_4^- anion all of the Al from a 0.0075 M solution is transformed into the gel at pH 4.7 to 4.8. No sol state of Al exists in the presence of this anion. The complete precipitation of Fe of the same molar concentration in the presence of SO_4^- anions takes place at the zone of pH 3.2 to 3.8. There is a sol state of Fe in the presence of the SO_4^- anion. Upon the removal of electrolytes by dialysis all of the Fe is transformed into the gel state. These conditions preclude the existence of Al or Fe in the presence of the SO_4^- anion.

2. In the presence of the Cl anion, complete Al precipitation from a 0.0075 M concentration of Al_2O_3 takes place at pH 5.4. Molecularly dispersed Al may persist almost up to the point of complete precipitation. Similar results in respect of complete precipitation were obtained with the Fe colloid in the presence of the Cl anion. The molecularly dispersed Fe disappears as soon as the gel begins to form. Removal of electrolytes does not convert the sol into the gel as in the case with Fe colloids in the presence of the SO_4^- anion. Apparently the differential adsorption of the SO_4^- and Cl anions and their electrostatic behavior is responsible for the phenomena observed.

3. In the presence of the NO_3^- anion, Al is completely precipitated at pH 5.8 to 6.0. Fe is precipitated completely at pH 5.4. As with the Cl anion the formation of the gel excludes the molecularly dispersed particles. The

removal of the electrolytes does not readily induce gel formation: the colloid remains in the sol state; only after prolonged standing, heating, or at times shaking will some gel be formed.

4. In mixtures of anions the properties of the divalent or trivalent anions control the states of aggregation of the Al and Fe colloids.

5. The possibility of Al and Fe in solution is discussed and the conclusions are that under normal soil conditions the inorganic anions will preclude their presence. There is the possibility of Al being in solution from the dissociation of the electrolytic-like colloid—the Al-silicate complexes in the soil. Iron is probably supplied to the plants by the dissolving action of the organic acids and probably other organic solvents.

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THE PERPETUALLY FROZEN SUBSOIL OF SIBERIA¹

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The perpetually frozen subsoil, found extensively in Siberia, forms one of the most interesting phenomena of the lands of Northern Asia. In the perpetually frozen, also called "ever-frozen," subsoil the temperature never rises above 0°C. Throughout its mass, except at its lower surface and once during the year at its fluctuating upper surface, the temperature constantly remains some degrees below zero and water is present only in the form of ice.

The first information relative to the perpetually frozen subsoil of Siberia dates from the end of the seventeenth century (1676-1692) but not until about the middle of the nineteenth century, when Middendorff, a member of the Russian Academy of Science, made a journey into northeastern Siberia, was any real scientific investigation or exploration of the phenomenon undertaken. Since that time many scientists and explorers have contributed to the elucidation of the questions connected with it. The investigations were especially numerous and fruitful at the end of the nineteenth century and in the very beginning of the twentieth, following the construction of the great Trans-Siberian railroad and the more intensive colonization of eastern Siberia.

The most recent contribution to this question is the monograph of Soumgin (9). Although the subject is given a very detailed treatment in this interesting book a complete explanation of this natural phenomenon still seems far away. Probably this is due largely to the more or less local character of the explorations, which have been made almost entirely in northern Asia in the non-glaciated area. Only the most meager information has come from other northern lands, Canada, Greenland, and Alaska.

The purpose of this paper is to call the attention of Canadian and American explorers to the importance of the phenomenon. In the author's opinion, it will be only through the investigation of the entire phenomenon over the entire northern portions of the northern hemisphere that the solution of this mystery of nature can be attained. Explorations in the glaciated region of northern Canada are likely to have decisive significance.

DISTRIBUTION OF PERPETUALLY FROZEN SUBSOIL IN EURASIA

This phenomenon extends over a vast region in Asia (fig. 1) covering more than three million square miles—almost as large an area as the United States

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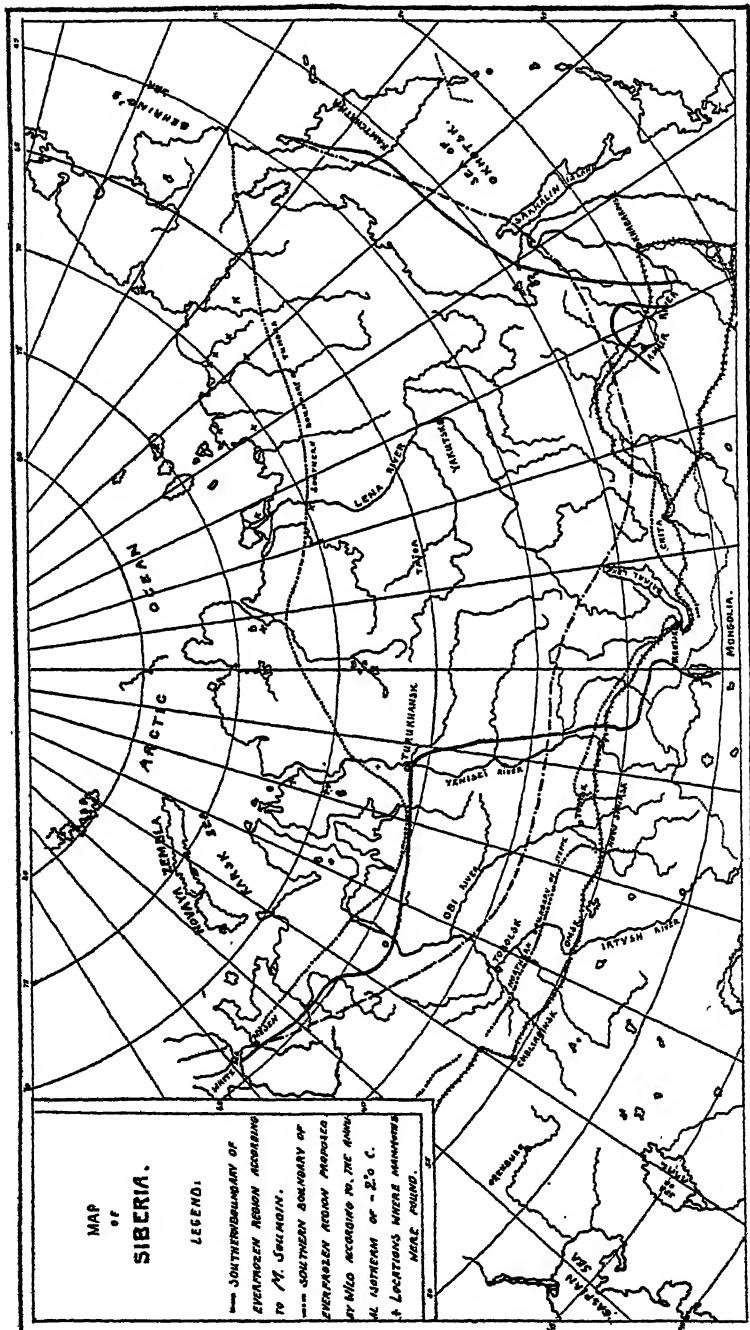


FIG. 1. MAP OF SIBERIA SHOWING BOUNDARY OF THE PORTION IN WHICH THE EVERFROZEN LAYER HAS BEEN FOUND

and Alaska together. On the north it reaches the Arctic Ocean and at several places near the coast, ice has actually been found on the bottom of this sea. Its southern boundary is very irregular. Beginning on the west in European Russia near the town of Mesen, on the coast of the White Sea, it closely follows the 65th parallel of latitude, eastward to the Yenisei River in Siberia, where it turns sharply southward and continues in this direction to a point about 150 miles west of Lake Baikal, in south central Siberia. There it crosses the Chinese boundary and extends for some distance into Mongolia, to about the 49th degree of latitude, corresponding to the southern boundary of Canada west of the Province of Ontario. To the north and east and extending to the Arctic and Pacific Oceans, the subsoil of Siberia is continually frozen below a depth of 4 to 10 feet from the surface, except for a relatively narrow strip along the Sea of Japan and the Sea of Okhotsk, consisting of the district between Vladivostock and Khabarovsk, the lower part of the Amur River basin and the southern portion of the Kamchatka peninsula. This vast area extends more than two thousand miles from north to south and several thousand miles from east to west.

UPPER AND LOWER LIMITS OF THE PERPETUALLY FROZEN LAYER—ITS THICKNESS AND TEMPERATURE

The depth to which the soil thaws during the warm but short summer does not depend entirely upon the latitude, but rather upon the character of the vegetation and the physical properties of the upper layers of the soil. Close to the Arctic Circle and on the 55th parallel of latitude it is more or less uniform. The mosses, especially sphagnum, offer the best protection from melting. During the whole summer, ice and frozen soil are commonly found a foot or two beneath the moss and sometimes even within a few inches of it. The sands and other drier soils, especially if they are not covered by a thick growth of grasses, thaw out to greater depths, varying from six to ten feet, while the loams and clays do not thaw to more than three to five feet.

In general, the thickness of the frozen layer varies from north to south, being thicker in the north, where it reaches hundreds of feet. Exact measurements have not been made as to the maximum thickness but the following data have been secured at the city of Yakutsk, which is situated on the Lena River, and near the 65th parallel, close to the center of the frozen region. There several deep wells were dug in the hope of securing a supply of good drinking water for the city. One of these wells is 382 feet deep and the temperature of the ground near the bottom of it was -3°C . From computations based upon determinations of the temperature throughout the whole depth of this well it is concluded that the general thickness of the frozen layer at Yakutsk must be between 550 and 650 feet. Towards the southern boundary the thickness gradually decreases, several points having been found between the 50th and 55th parallels where the frozen layer was only from 100 to 250 feet thick.

The temperature of the ever-frozen ground was studied most extensively at a depth of from 25 to 30 feet from the surface. In a few places it was examined at a greater depth, namely in the deep wells of Yakutsk, by Middendorff (2). This explorer, who had devoted much time to explorations in northeastern Siberia, made very careful temperature observations during the period from April 5, 1844, to June 18, 1845. In the deepest well, the so-called "well of Shergeen," he found the mean annual temperature for different depths as given below:

DEPTH feet	TEMPERATURE °C.
7	-11.17
15	-10.22
20	-10.17
50	- 8.28
100	- 6.56
150	- 5.78
200	- 4.84
250	- 4.17
300	- 3.89
350	- 3.44
382	- 3.00

He also found that below a depth of between 50 and 100 feet the temperature remained very constant during the whole year, while at a depth of 20 feet it varied from -13° to $-7.7^{\circ}\text{C}.$ and in the layers above this the fluctuations were considerably greater.

The annual minimum of the temperature of northeastern Siberia occurs in January. The minimum in the well at a depth of 7 feet from the surface, $-14.1^{\circ}\text{C}.$, was found in March; at 15 feet, $-14^{\circ}\text{C}.$ in April, and at 20 feet in May.

According to the ten-year meteorological records of the Bomnak Experimental Station, in the province of Amur, at a depth of 2.8 meters the mean annual temperature is $-0.9^{\circ}\text{C}.$ the maximum usually occurring in January and the minimum in the early part of May. Thus at this depth both the annual maximum and the annual minimum occur approximately five months later than at the surface.

Middendorff's data pertaining to the observations on the temperatures at varying depths in the wells have been more or less severely criticised from time to time by different investigators, notwithstanding the careful planning characteristic of his explorations and investigations.

It must be pointed out that the Shergeen's well was dug entirely by hand and so difficult was the work that it took almost 10 years to reach the depth of 382 feet. It was begun in 1828 and at the end of the first year it was only 42 feet deep; in 1829 it reached 60 feet; in 1830, 91 feet; at the end of 1836, 306 feet; and in 1837, on reaching the depth of 382 feet, the work was discontinued.

The object in starting the well had been to secure a supply of good drinking water for the town but on failing to secure water during the first season Sher-geen had the work continued, in order to satisfy his curiosity as to how deep the frozen layer extended.

Middendorff's determination of temperatures in the well was made in 1844 and 1845, seven years after the lowest portion had been completed. Suspecting that the temperature near the face of the well had, through the influence of the air temperature, altered more or less during the period elapsing since the completion of the digging, Middendorff, at each point where he determined the temperature, made small horizontal holes extending 7 to 8 feet back from the face of the well. In each of these he inserted two thermometers, one at a distance of 1 foot from the face, and the other at a distance of 7 feet. He satisfied himself that the thermometers at the 7 foot points indicated the original temperatures of the frozen ground and that the temperature at this distance from the face of the well had not been modified by the presence of the well.

Whether his method gave the actual original temperatures is, of course, not known. For this reason his data have been criticized, and his deductions as to the general thickness of the ever-frozen layer in this area may be open to question. There is, nevertheless, no question as to the lack of uniformity of the temperature of the ever-frozen ground throughout its whole thickness. As a rule it gradually increases with increase in depth from the level at which it remains practically constant throughout the whole year. Above this level the temperature varies, the variation corresponding to the seasonal fluctuations of the air temperature.

THE PRESENT STAGE OF THE PHENOMENON

A number of Russian explorers of the ever-frozen ground endeavored to determine the general state of development of the phenomenon—whether its southern boundary is steadily extending southward and its thickness at any given point is increasing or vice versa. Up to the present time no definite information concerning this has been secured and the question still remains unanswered, but it seems probable that the phenomenon decreases gradually and that its southern boundary has moved northwards. The strongest argument in favor of this idea is the discovery, in at least sixteen places along the southern boundary, that the surface of the perpetually frozen layers lies at a greater depth from the surface. As an example, a frozen layer, almost 70 feet thick, was found near Petrovsky Zavod in the Trans-Baikal province (51.17 degree of latitude) with its surface at a depth of approximately 103 feet (9, p. 69). It is evident that such a layer has no connection with contemporary freezing of the surface soil every winter and can be explained as an inheritance from the remote past.

Another argument in its favor is found in the ecological investigations of the

tundra landscape's origin. The botanists' deduction (10) is that at the time of the great glaciation the tundra occupied a much larger area than at the present time and probably the very extensive northern tundra was closely connected with the alpine tundra of the central Asiatic mountain region. Afterward, the connection between that on the northern plains and that in the mountains was severed, and the southern boundary of the former moved northwards, with the steppe from the south advancing to replace it, during the xerophytic period of the continental epoch. Doubtless the perpetually frozen ground is the most typical phenomenon for the tundral physiographic landscape and it is probable that the southern boundary of this must move northwards following the retreat of the tundra.

Such a northward movement of the deep lying frozen layers would require much more time than the transformation of the landscape—the natural conditions on the surface. Therefore, while the tundra of Eurasia has now retreated almost entirely within the Arctic Circle, perpetually frozen layers still extend far to the south in Siberia. Accordingly we now find over the ever-frozen subsoil not only tundra landscape but also typical steppe with chernozem soils, westward from Baikal Lake, and even chestnut soils, in the Trans-Baikal province as well as in northern Mongolia (Fig. 1).

TWO HYPOTHESES AS TO ORIGIN OF THE PHENOMENON

In explanation of the origin of the perpetually frozen subsoil two principal hypotheses have been advanced by Russian scientists.

Climatic hypothesis

One hypothesis is that the phenomenon is a result of contemporary climatic conditions. The southern boundary of the region coincides more or less closely with the line north of which the mean annual temperature is everywhere considerably below 0°C. (fig. 1). In fact it is not higher than -2°C. and over a large area, as for example at Yakutsk, it is as low as -10°C. The supporters of this hypothesis maintain that the excess of annual cold can not disappear without any effect and that the volume of the ground which is frozen by the severity of the winter's low temperatures can not be wholly melted by the limited amount of the summer's heat. Accordingly every year some residue of this cold must remain, such "frozen residues" accumulating year after year and the frozen layer gradually increasing in thickness. This hypothesis was first proposed by Wild (13; 9, p. 99) who after extensive experiments, concluded that the mean annual temperature of the subsoil at a depth of 1 meter is approximately 0.9°C. higher than the temperature of the air, that the average temperature of the ground increases 2.97°C. for every 100 meters increase in depth, and finally that in the northern countries the zone of unvarying temperature lies at a depth of about 23 meters. After such deductions he derived the

following formula of the ratio between the temperature of the air (T) and that of the subsoil at a depth of 23 meters (t):

$$t = T + 0.9^\circ + 0.22 \times 2.97 = T + 1.6^\circ\text{C}.$$

It means that $t = 0^\circ$ when $T = -1.6^\circ\text{C}$. and, at places on the earth's surface where the mean annual temperature of the air is -1.6°C . or lower, the temperature of the ground at a certain depth can not rise above 0°C ., and hence below this the ground must remain perpetually frozen.

This strictly theoretical formula brought forth considerable discussion. It was pointed out that the protecting influence of the snow cover, the effect of the altitude above sea level, the climatical variations during the course of centuries and various other factors will influence the conditions mentioned above.

TABLE 1
Effects of depth of snow cover upon the temperature of the underlying soil at Bomnak, Siberia

YEARS	DEPTH OF THE SNOW COVER		MEAN TEMPERATURE OF THE AIR		MEAN TEMPERATURE OF THE SOIL AT THE DEPTH OF 1.5 M.	
	January cm.	February cm.	January °C.	February °C.	March °C.	April °C.
1912						
1913	13	17	-32.4	-22.2	-5.9	-4.3
1915						
1914						
1916						
1917	28	30	-30.9	-23.6	-2.7	-2.1
1918						
1919						

The value of the protection offered by snow is shown by the following data taken from the records of the Bomnak meteorological station. For 1912, 1913, and 1915 the snowfall was very light, but [for 1914 and for the period from 1916 to 1919 it was very deep. The effects of the snow upon the cooling of the soil are shown in table (9, p. 158). The temperature of the soil at a depth of 1.5 m. in March and April corresponds to the temperature of the air in January and February, the retardation of two months being due to the slowness with which the cold penetrates the upper layers.

Glacial hypothesis

According to the other hypothesis the ever-frozen ground is an inheritance from the glacial period. It is known that very little of Siberia was covered by ice at the period of the Great Glaciation and because of this the supporters of the second hypothesis hold that the area unglaciated, and so left unprotected by ice, was at that time frozen to a great depth.

The principal argument in favor of the second hypothesis has been provided by the discovery in the frozen ground of bodies of ancient mammoths and rhinoceroses, many of which were so well preserved that the natives used the grease obtained from them (9, p. 65). The stomachs of these animals contained undigested food which was in such good condition that it was possible to determine the species of plants that the animals had eaten just before their death (7). It is evident that the bodies of these animals could have been thus preserved during many thousands of years only under the protection of permanent frost. It means that at the time these animals succumbed the subsoil was already frozen and has so remained up to the present.

It appears probable that each hypothesis is partly correct and partly incorrect. There is no question that the existence of the ever-frozen ground at the present time depends upon the contemporary climate and that the annual excess of the loss of heat from the surface into the atmosphere over the amount of heat annually received by the same surface from the sun has a definite significance. Although it is true that the discovery of the bodies of mammoths proves that the ground has been frozen for a long time, it does not dispose of the rôle played by pre-existing climatic conditions. Probably the conditions prevailing during the glacial period were more severe, and the freezing was considerably more rapid, than at present, but even so the appearance of the frozen subsoil then or later must be regarded as a function of the climate.

If the origin of this phenomenon is dependent upon the absence of protecting glacial ice in eastern Siberia during the glacial period, and if the Great Glaciation in Europe and North America occurred simultaneously with the forming of the ever-frozen ground of Siberia, then the question may be asked as to why the ice sheets were melted while the frozen ground of Siberia, the so-called "continental facia" of the glacial period, remains to the present time. This, of course, must be explained by a change of climate in the glaciated areas of western Europe and northern North America with little or no change in that of Siberia. It means that the present climate of much of Siberia is favorable for the existence of the ever-frozen ground.

There is no reason to assume that the climate during the Glacial Period was not more severe than the contemporary one, even in Eastern Siberia, in parts of which a temperature of -62° to -59°C . is a common phenomenon of every winter, but it may be pointed out that there are no reasons for minimizing the contemporary climate's rôle in the development of ever-frozen ground, even if it be accepted that the ever-frozen ground is a geological formation.

A very interesting deduction has resulted from the discovery of the mammoths at the different places indicated in figure 1. The finding of at least thirty of these has been reported up to the present, but not in all cases have entire bodies been found, some of the finds reported being of only parts of a body—the head, or a leg with flesh, skin, and hair attached. The circumstances under which the animals died have been contributing factors to the state of preservation. In several cases the investigators had an opportunity to

re-establish in every detail all the circumstances under which the animal had perished. As an example, reference may be made to a part of an article written by the geologist Volossovitch (9, p. 220) in which he describes the discovery of the Sanga Yurakh mammoth. His statement regarding this follows:

The mammoth perished in the summer, because it had a thick wool-hair on its hide. As he approached the river bank, where the frozen ground with incrustations of ice was under the mud, he became stalled in this mud. For a long time he kept trying to raise his right hind leg in an attempt to free himself, but without success. Finally he fell down with his left side exposed. Little by little the mud covered his body, but before it became totally concealed the savages removed as much of the carcass as they could. Those parts of the body which were nearest the frozen layer from the very beginning were preserved in the best condition.

In connection with the various discoveries of these mammoth remains it should be emphasized that not one was made as the result of any special search, but every one was more or less accidental and made usually by natives and not by scientists. The scientists usually heard of a discovery only indirectly and so only after considerable time had elapsed from the finding of the carcass or part of one. The occurrence of these bodies clearly indicates the magnitude of a rich field for paleontological research. The ever-frozen subsoil contains, of course, not only the bodies of mammoths, but the remains of many other prehistoric animals.

PHENOMENA OF THE SURFACE SOIL DEPENDENT UPON PRESENCE OF PERPETUALLY FROZEN LAYER

During the period from 1909 to 1912 the author had the opportunity of investigating the soils in northeastern Siberia and at that time studied the frozen subsoil and especially the surface layer above this, which thaws during the summer. There are many phenomena of the perpetually frozen ground but only some of those that came under his personal observation will be dealt with here.

Suffusion process

It has been pointed out, that the rapidity with which the soils thaw during the summer depends upon their texture and the character of the protecting vegetation. During the warmer portion of the year, therefore, the upper surface of the frozen layer is very uneven. The water cannot percolate through it, because the first water reaching it seals with ice all cracks in the frozen subsoil. All water derived from rain and snow and the thawing of the subsoil accumulates above the ever-frozen layer, often in such quantities as to form a liquid layer under the dry thawed surface. Such a condition favors the extensive development of swamps not only in the lowlands but upon the mountain slopes as well. During his travels, the author crossed at several places the high Yablonovi Mountain ridge, separating the provinces of Yakutsk and Amur, and

everywhere, with the exception of the rocky summits, this ridge was covered with peaty swamps. In some places the slopes were so steep that it was nearly impossible for the horses to climb them, but nevertheless they had a viscous peaty covering, which on the frozen subsoil, provided a very slippery footing.

Often in the summer a layer of water was found under the firm and apparently dry crust of the surface soil, and frequently it was found creeping down into the lower levels. Sometimes the pressure exerted was so great that the water would crack the dry crust and the liquid mud would then pour out over the surface. In other cases a process, genetically similar to this, caused the development of formations of another kind. The layer creeping down was too dense to pour but after bursting through the surface soil it formed small convex mounds, which under foot were resilient like elastic cushions.

This phenomenon is known in Russian literature as a "suffosion process", and has been examined by Prokhoroff (5) in the province of Amur and by

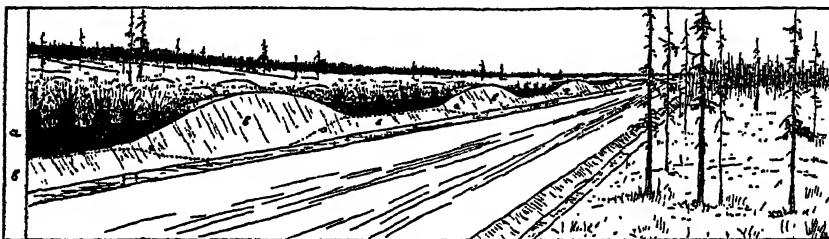


FIG. 2. "SUFFOSION COMPLEX" AS IT APPEARED ALONG A ROAD CUT THROUGH A COMPLEX SWAMP IN AMUR PROVINCE

a, peat; *b*, mineral subsoil; *c*, surface of ever-frozen subsoil

Sukatcheff (8) in the province of Trans-Baikal. They describe a very unusual soil complex, which occupies the large gentle slopes in this region.

The soil is mostly peat which is covered with hillocks of carex. Through the surface penetrate numerous hummocks of subsoil in the form of convex mounds. The total surface covered by these mounds is frequently more than one half the surface of the whole area. They do not rise on the average more than two feet above the level of surrounding swamp and usually have very irregular shapes (fig. 2). The most recent suffosion knobs are almost bare of vegetation while even the oldest are but very slightly podsolized.

The bare surface of the suffosion convexes hastens the melting of the subsoil and therefore causes marked irregularities of the surface of the ever-frozen layer beneath the complexes. For each convex occurs a corresponding shallow depression in the frozen surface. Because of this it can be readily understood that any attempts at farming these soils would meet with great difficulties.

Soil blisters and ice caverns

In the autumn and winter, after the soil has frozen at the surface the water layer is found lying between this frozen surface crust and the ever-frozen sub-

soil. Under the influence of the very low temperature a high pressure is created by the expansion of the freezing water and this exerts such a force that in places the surface layer is raised like a gigantic water blister, with all the buildings and trees that may be on the surface. The author observed mounds of this kind which were more than twenty feet high, all being full of water (plate 1). Under the pressure, fissures are formed and the water spurts out in geyser fashion. In several mounds the surface was intentionally punctured near the base thus allowing the water to escape. After this the mounds were found to contain large caverns beneath the soil, which was supported by massive vaults of clear ice (fig. 3). The caverns were so large that one could walk upright within them without difficulty. Some of them were as much as six or seven feet high and almost thirty feet in diameter. The icy caverns were covered with a layer of soil two or three feet thick bearing large larch trees, standing at right angles to the rounded surface of the mound and not vertical, as they were before the sudden growth of this little hill (3, p. 50-74).

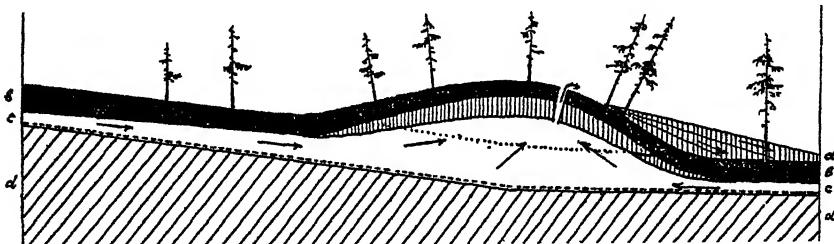


FIG. 3. CROSS-SECTION OF A SOIL BLISTER

a, accumulation of clear ice, both on the surface and under the raised frozen surface soil; *b*, frozen surface soil; *c*, water in liquid form; *d*, ever-frozen subsoil.

Winter regimen of the river valleys

The streams and rivers of this region frequently freeze to the bottom and the ice forms dams across the river bed. In such cases the water coming from the upper parts of the river seeks outlets through the soil adjacent to the stream and often appears on the surface of the ground far away from the banks of the river. These places are very dangerous to travellers of the Siberian *taiga* (northern forest), in winter, because of the deep water, and in summer because of the blocks of ice remaining. In winter, when the temperature often reaches -45° to $-50^{\circ}\text{C}.$, such places are full of water. The lower the temperature the higher will be the pressure in the water layer above the ever-frozen subsoil and consequently more and more water will be forced to the surface. In order to escape the treacherous water-soaked snow, which frequently covers several square miles, it is very common for travelers to go many miles through deep snow, breaking paths through the virgin forest.

An investigator of the Academy of Science, G. Maidel, who visited the

northeastern part of the Yakutsk province in 1868-1870, in his report described in detail one of these formations, which covered more than forty square miles and in some places was more than seven miles in width. It was caused by the Kyra and Nekharan rivers together with their tributaries (1).

During the long winter the water freezes little by little, forming layers of ice one above the other, which are pushed together, forming almost impassable barriers. The summers are not long enough and the heat from the sun's rays is not sufficiently penetrating to melt entirely all the ice that has accumulated during the winter, with the result that varying amounts of ice remain until the following winter. In several places at the middle of August the author saw huge blocks of transparent blue ice which were more than ten feet thick and walked along these for more than a quarter of a mile. These summer fields of ice, or "taryn", as the natives call them, form one of the most fantastic and contrasting pictures in the landscape of eastern Siberia.

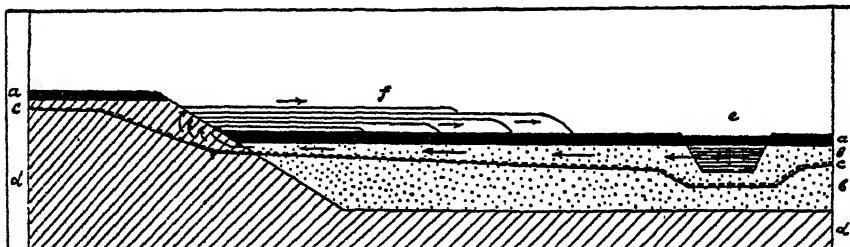


FIG. 4. DIAGRAM TO EXPLAIN THE "TARYN"

a, frozen surface soil; *b*, alluvium of the river valley; *c*, surface of the perpetually frozen layer; *d*, country rock; *e*, river, *f*, winter accumulation of ice on the surface, most of which remains through the summer.

Podyakonoff, a mining engineer, who first studied the dynamics of this phenomenon offered the following formula, which shows the relation between the energy of the phenomenon (*R*) and the attributed natural conditions:

$$R = P \frac{c}{d} Q \frac{a}{M + N}$$

where *P* = the force of the frost.

c = heat capacity of the alluvium.

d = thickness of the snow layer.

Q = quantity of liquid water (unfrozen) in the river bed and unfrozen deposits.

a = width of the valley.

N = the cross section of the open river bed.

M = the cross section of the unfrozen deposits in the valley, through which the water is pressed from the bed (4; 9, p. 275).

Mechanical effects upon soil texture

Probably, in the region having the ever-frozen subsoil, the periodical freezing and thawing of the large quantities of water which occur in the upper horizons of the soil has a stronger influence upon soil development than either the lowering of the temperature by the frozen subsoil, which would cause a decrease of biological activity, or the formation of the layer of liquid water above the impenetrable frozen surface.

The freezing and thawing of the water causes the separation of the soil particles, breaks the soil material asunder, and facilitates the removal of the finest material from the upper horizons and its accumulation just above the permanently frozen surface. In many places it was observed that the assorting of the soil particles had gone so far as to completely remove the finer mellowing material, leaving only coarse stony fragments on the surface. Even these were assorted, the individual fragments being coarsest on the surface and becoming smaller and smaller with increasing depth (3).

A considerable number of areas were found which were covered by layers of debris of varying thickness, either entirely bare or covered only by a thin layer of moss. These were most pronounced in those places where the soil blisters and ice caverns were of most frequent occurrence.

The freezing of the water causes a coarse lamination, due to alternate thin lamellae of clear ice with lamellae of soil compressed between them. The average thickness of the icy lamellae, which are usually in the form of large horizontal lenses, is from 0.1 to 0.4 inch. The clearest expression of this lamination was found in the peats, but it was observed also in the mineral soils. The occurrence of such lamellae in the upper horizons of the soil raises the question as to whether a similar structure found in other soils, such as the podsol, swamp, and alkaline soils, depends upon the periodical freezing and thawing of these horizons, especially in the fall when they are wet and when frosty nights alternate with warm days.

AGRICULTURE OVER THE PERPETUALLY FROZEN SUBSOIL

The presence of the ever-frozen ground, as such, is something that would not be expected to attract many to agricultural pursuits, but nevertheless in some respects it has decided advantages. According to the settlers the crops never suffer from drought. The presence of the frozen subsoil and the continuous melting of it during the growing season supplies the crops with sufficient moisture. This is a very important factor because of the extreme continental climate, with the short, very hot and dry summers during which the frozen subsoil serves as a reservoir of moisture.

The days of long sunshine are the second favorable factor in the northern region. The sun shines from 21 to 22 hours out of every 24 during May and June and for this reason the northern region sometimes has an advantage over the more southern provinces. In 1912 the author observed excellent crops ripe

in the fields around Yakutsk, whereas three weeks later near the city of Irkutsk, more than 12 degrees of latitude southward, he found the crops were still immature, and they were soon after ruined by frost.

The population in northern Siberia, aside from several thousand Russians, consists mainly of Tunguses and Yakuts. The former occupy all of northern Siberia and to the south the area between the Yenisei and Lena rivers. They are real nomads and their only employment is hunting. They have no conception of agriculture and most of them have never seen grain or even tasted bread.

The Yakuts occupy the large province of Yakutsk and are in closer connection with Russian farmers. Gradually they learn and practice the agriculture of their Russian neighbors.

In 1909 and 1910 several fully equipped agricultural experimental stations were established in the province of Amur, in which, next to gold mining, agriculture forms the most important industry. These are located within the boundaries of the perpetually frozen subsoil. In the more severe climate of Yakutsk, agriculture is in the most primitive stages. There it commenced with the settlement of farmers from European Russia about 50 or 60 years ago. The Yakutsk region at one time was used by the government as a place for religious exiles. At one time a colony of Doukhobors, a religious sect, the adherents of which are now living in parts of Canada and California, lived here. These industrious and persistent farmers not only overcame the natural severities of the virgin taiga but with great difficulty modernized their farms with agricultural machinery, in spite of the fact that the nearest railroad lay some 2000 miles away. Rye, oats, barley, and wheat and many kinds of vegetables grow remarkably well in Yakutsk, notwithstanding the relatively short growing season, which is limited to about 100 days. Probably one of the most surprising discoveries of the author in Siberia was that of an American harvester in use on a large farm in the vicinity of Yakutsk.

The Yakuts' system of farming is still very primitive and their fields are very small, seldom larger than one acre. Their main crop is barley, from which flour is made by grinding the grain by hand between two stones. These beginnings of agriculture can be found in many places throughout the vast, severe *taiga*.

In northeastern Siberia there are many good pastures and meadows bordering countless small lakes and the small streams, from which good hay may be secured. Dairying is much more successful than grain raising, with the Yakuts. Milk products, mostly butter and cheese, are their principal food. The butter is usually eaten alone as a dish by itself and not with bread or any other vegetable food. In keeping it fresh no difficulty is experienced, as a hole 5 or 6 feet deep reaching into the perpetually frozen subsoil, affords an excellent natural refrigerator.

OCCURRENCE OF PERPETUALLY-FROZEN SUBSOIL IN NORTH AMERICA

But few references have been found to the occurrence of a perpetually frozen layer in North America, but there is reason to believe that it covers a considerable part of Alaska and the districts of Mackenzie and Franklin in Canada and perhaps part of the most northerly portions of the provinces of Manitoba and Saskatchewan. Most of the references have been found in reports of J. B. Tyrrell of the Canadian Geological Survey regarding the Klondike and the lands west and northwest of the coast of Hudson Bay. It is

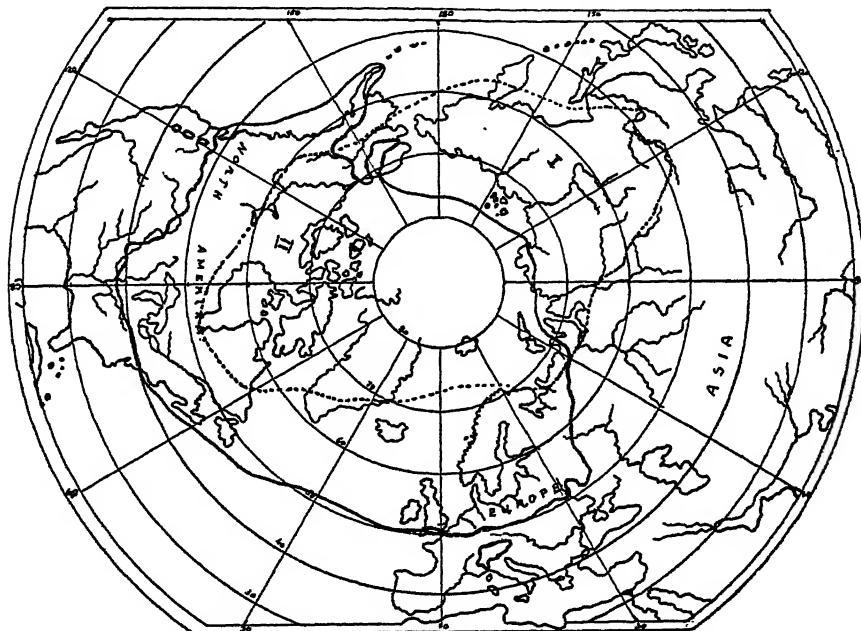


FIG. 5. MAP OF NORTHERN HEMISPHERE

—Boundary of Glaciation. ———Boundary of area of perpetually frozen ground. I. Explored area. II. Unexplored area.

possible that both the above mentioned districts are situated near the southern boundary of the continuous permanently frozen area of the North American continent. Corresponding to the annual isotherms, the southern boundary of such an area in North America should be expected to follow the southern boundary of the former district of Ungava from Labrador to Hudson Bay, thence along the southwestern coast of this bay as far as the 60th parallel, then along this to about the source of the Yukon River, and then along this and the Tanana River to the vicinity of Nome (fig. 5).

It is probable that the question as to the origin of the ever-frozen ground can be best answered by investigations undertaken in northern Canada, most of

which, at least, was covered by the great ice sheet during the Glacial Period. If no permanently frozen ground were found in this glaciated region with a climate now similar to that of eastern Siberia it certainly would prove that the ice sheet served as a protective cover and that the severity of the contemporary climate is not sufficient to bring about the formation of this perpetually frozen subsoil. On the other hand if the ever-frozen ground should be found in this glaciated area, it would support the hypothesis that freezing took place after the deposition of the drift and the recession of the ice, that the absence or presence of glaciation did not influence the development of this phenomenon, and that its origin is not necessarily associated with the Glacial Period.

SUMMARY

The permanently frozen lands of Asia, Europe, and North America, including the islands situated northward from the Arctic Circle, form an original physiographic zone around the North Pole.

Nearly three million square miles in northern Asia are occupied by the region of perpetually frozen subsoils. In northern Europe there is but a relatively small area lying between the White Sea and the Ural Mountains northward from the 65th parallel.

In North America perpetually frozen subsoil has been reported from Alaska, Northern Canada, and Greenland but its southern limit is not known.

The thickness of the permanently frozen layer in Asia and Europe, which is to be regarded as a geological formation, varies from several hundred feet in the north to 50 feet or less in the south. During the summer the surface thaws to a depth of about 6 inches to 10 feet.

The temperature of the frozen layer is lowest near the surface and gradually increases with depth.

Two hypotheses have been advanced in explanation of its origin, the one climatic and the other geological.

If the phenomenon is an inheritance of the Glacial Period it can be regarded as now in a stage of gradual decrease proceeding toward its final disappearance. If, on the other hand, it depends upon the severity of the contemporary climate, it is a stable phenomenon, and the area may be even increasing its boundaries.

The exploration of this region of the permanently frozen ground in the glaciated area in Canada and Alaska, and especially along its southern boundary, would bring more definite information as to its origin and the relation between the permanently frozen layer and glaciation.

The presence of frozen subsoil causes in the upper layers of the soil several dynamic processes which are not found under any other conditions. As a factor of soil formation and development it favors the extensive development of swamps and the growth of mosses, the assorting of soil material with the removal of the finer particles from the upper horizons, and the development of the soils complexes.

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² Because of lack of access to most of the original sources, except Soumgin's monograph and Nikiforoff's paper, all references in this paper are made according to Soumgin's data. The data concerning the meteorological observation on the Bomnac Experiment Station are taken from the same source. In his monograph Soumgin cites 116 titles of books and papers published in Russian, dealing with the perpetually frozen subsoils.

PLATE 1

FIG. 1. Typical soil blister, with the slopes still covered with ice formed from the water which had spurted out.

FIG. 2. View of ice-lined cavern.

PERPETUALLY FROZEN SUBSOIL OF SIBERIA
CONSTANTIN NIKITOROFF

PLATE 1



FIG. 1



FIG. 2

PLATE 2

FIG. 1. Tamarack tree on the summit of a blister, split when the blister broke.

FIG. 2. Summer view of the remains of a blister, the central part having fallen.



FIG. 1



FIG. 2

BOOK REVIEWS

Fortschritte der Mikrochemie in ihren verschiedenen Anwendungsbereichen (*Advances of Microchemistry in its various applications*). Edited by GUSTAV KLEIN and ROBERT STREBINGER. Franz Deuticke, Leipzig and Vienna, 1928. pp. 436.

This book presents in a condensed form the present status of the subject of microchemistry and its application to inorganic and organic analysis.

The wide scope of the subject can be readily recognized from a glance at the various chapters which make up about one-third of the book: Quantitative inorganic microanalysis, by R. Strebinger; Quantitative organic microanalysis, by E. Philippi; Qualitative analysis by microcrystallography, by G. Deniges; Microchemistry of minerals, by P. D. C. Kley; Colloidal chemistry and its relation to microchemic analysis, by M. Spiegel-Adolf; Plant histochemistry, by G. Klein; Animal histochemistry, by V. Pratzelf; Application of microchemical methods in the analysis and investigation of drugs and poisons, by R. Waricky and A. Mayrhofer; Progress of microchemistry during 1915-1926, by A. Benedetti-Pichlet.

The other two-thirds of the book are devoted to the various methods used in general and special microchemistry. Of special interest to the student of soils are the sections dealing with the methods of sedimentation, titration, gas analysis, mass determination, surface tension, viscosity, qualitative and quantitative methods of analysis of inorganic and organic substances, biochemistry, etc.

The book has very few illustrations and no indices, but it has a very extensive bibliography, placed conveniently in the form of footnotes.

S. A. WAKSMAN.

Kurs Poichkoviedienia (Textbook of Soil Science). By C. A. ZACHAROV. Gosizdat, Moskau and Leningrad, 1927. pp. 440.

The author of this book, the well known Russian pedologist Professor Zacharov, of the Agricultural Institute at Krasnodar, has summarized, in a very concise manner, the current ideas of the Russian pedologists on the subject of soils as an independent science. The author has selected, in a most objective manner, the necessary data from the mass of material, facts, hypotheses, and theories relative to the discipline under consideration, and has prepared a book, which can be of great use not only to the soil scientist, but also to the general student specializing in agronomy and soils, and to all those interested in sciences related to soils.

The author adheres throughout the book to the principle laid down in 1878 by B. B. Dokutchairov, the originator of the modern genetic treatment of soil science, that "the soil is a special independent natural-historical body," similar to a rock system, a mineral system, and even an organic system.

The nature of the book can best be summarized by its table of contents: Preface; Introduction, The soil, soil formers, and soil formation; I. Soil morphology, including chapters on soil color, soil structure, soil horizons and the soil skeleton; II. The soil mass, including the mechanical and mineralogical composition of soil, chemical composition of soil, absorbing capacity of soil, physical properties of soil, and the soil organisms or the soil "edaphon;" III. Soil formation or soil genetics, with chapters on weathering, soil forming agencies, soil formation (pedogenesis), etc.; IV. Soil classification; V. Systematic study of soils, with descriptions of different soil types; VI. Geography of soils, containing a discussion of the horizontal soil zones and vertical soil zones; VII. The life of the soil, with chapters on soil temperature, moisture, aeration, solution, plant nutrients, absorbing complexes, and microbiological activities.

A detailed bibliography of 50 to 100 references is given at the end of each section. Three large tables on soil classification and a colored map of the soil zones of U. S. S. R. are included in the book.

S. A. WAKSMAN.

THE SELECTIVE ABSORPTION OF INORGANIC ELEMENTS BY VARIOUS CROP PLANTS

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The experiments described in this paper were undertaken with the object of adding to the information obtained in previously reported experiments (3) and obtained by other investigators, regarding the selective action of different plants, as measured by the proportions in which they absorb different elements from cultural solutions and soils. In the experiments reported in this paper, no attempt was made to study the various factors influencing the absorption of inorganic elements by plants, which have been discussed elsewhere (1, 2, 3, 4), the object being simply to determine characteristic differences in absorption of various plant species.

For these experiments it was thought advisable to take common crop plants which under ordinary field conditions are believed to differ considerably in composition, and to grow them under carefully controlled greenhouse conditions, in order to find out whether the differences are really characteristic or simply the result of different environments.

An important feature of the experiment consisted in growing six plant species together in each culture solution container. An important advantage of growing the plants together is that the different species must then be growing in exactly the same solution at all times, even when the solution undergoes change because of the absorption of ions by the plants.

The soil-grown plants were also grown side by side in a single large box or tank, but it was thought that because of differences in the distribution of the roots, together with probable differences in the concentration of the soil solution in different parts of the soil mass, and possibly because of other factors, such as differences in carbon dioxide output from the roots, the several plant species might be absorbing from different solutions. In this connection it was suggested that the quantity of carbon dioxide given off from the roots in a soil may have an important influence upon the solubility of substances in intimate contact with the roots, particularly calcium and magnesium. In experiments previously reported (4) it was shown that there is a reasonably close correlation between the rates of transpiration and of root respiration when various crop plants are absorbing from a given culture solution, but that the rate of plant root respiration, as related to transpiration, is increased when the salt concentration of the culture solution is increased. It was considered that a

truer picture of the selective action should be obtained when these complicating factors were eliminated by growing the plants in a culture solution. In a culture solution free from solid particles diffusion is rapid, and it can be assumed that the plants are all absorbing from exactly the same solution.

The method of conducting the culture solution experiment was as follows: A standard culture solution employed in similar earlier experiments, and first recommended by Hoagland, was used; it has the following composition: 160 p.p.m. Ca; 185 p.p.m. K; 55 p.p.m. Mg; 720 p.p.m. NO₃; 105 p.p.m. PO₄; 215 p.p.m. SO₄. Iron was added at frequent intervals in the course of the experiment. Four 6-gallon crocks were filled with this culture solution. The solution was changed in the seventh week of the experiment, or ten days

TABLE 1
Composition of plants grown together in soil and in culture solution for 56 Days

KIND OF PLANTS	NUMBER OF PLANTS	AVERAGE WEIGHT PER PLANT		Ca	K	Mg	N	P
		Green tops	Dry tops					

Plants grown in culture solution

		gm.	gm.	per cent				
Sunflowers.....	19	24.4	2.32	2.18	5.01	0.640	3.60	0.560
Beans.....	20	15.9	2.25	2.11	4.02	0.594	3.62	0.546
Wheat.....	24	11.5	1.34	0.79	6.73	0.406	4.49	0.489
Barley.....	24	23.1	2.59	1.87	6.92	0.540	4.66	0.524
Peas.....	20	22.0	2.55	1.55	5.25	0.504	4.49	0.193
Corn.....	19	24.4	2.42	0.51	3.87	0.402	2.89	0.385

Plants grown in loam soil

		gm.	gm.	per cent				
Sunflowers.....	15	26.7	3.74	1.68	3.47	0.730	1.47	0.080
Beans.....	11	6.75	1.26	1.46	1.19	0.570	1.48	0.053
Wheat.....	18	9.0	1.85	0.46	4.16	0.225	2.26	0.058
Barley.....	10	17.5	3.4	0.68	4.04	0.292	1.94	0.125

before the plants were harvested. Test analyses showed that there was never any lack of essential elements. The seeds were sprouted in blotting papers, and, when transferred, were supported in holes bored through paraffined wooden covers. Five or six plants of each species were placed in each crock, and, as there were 6 species, each crock supported 30 to 36 plants. The set of plants analyzed was taken in preference to another lot grown similarly, because of the comparatively uniform growth of the different species, as shown by the weights given in table 1. When harvested, the wheat and barley plants had reached the shot blade stage, and two or three of the corn plants had produced tassels. The sunflower plants were rather irregular in size, and the peas and beans had produced some blossoms. The roots were

somewhat intertwined, and were not analyzed. Other details of the experiment are given in table 1.

The same kinds of plants were also grown at the same time, in the greenhouse, side by side, in a fertile Alberta "Black Belt" loam soil of about the following composition: 0.62 per cent N; 0.11 per cent P; 1.2 per cent Ca; 0.62 per cent Mg; and 1.5 per cent K. The wheat, barley, sunflowers, and beans were harvested at about the same stage of growth as the respective species grown in the culture solution, but the peas and corn were not analyzed, as they had made but poor growth and were not considered comparable with the other plants.

It will be observed that the absorption of inorganic elements was, in almost all cases, considerably greater from a standard culture solution than from the loam soil. This indicates that the concentration of the soil solution was not so great as that of the culture solution. Hoagland (1) found, in experiments with barley, that the concentrations expressed in percentages and total quantity of nitrogen and potassium per plant, were decidedly increased in the plant tops with increasing concentrations of nutrient solutions. Other experiments (3) show that increasing the salt concentration of the culture solution causes, as a rule, increased absorption of the salt ions by the plants.

It will be observed that in addition to the absorption from the culture solution being greater than from the loam soil, the variability in composition between different species of plants was greater for plants growing together in the loam soil than for plants growing together in the culture solution. The general tendency of the culture solution was to produce a more uniform absorption. There are, however, certain characteristic differences in the absorption of different plant species, which will be discussed later. Other experiments previously reported (3) also showed that the absorption of different plant species growing together in this culture solution was more uniform than that of different species growing together in a clay loam or adobe soil.

If the calcium content of the plants grown in the culture solution is compared with that of plants grown in loam soil, the greatest difference is found in both solution and soil, between wheat and sunflowers. Comparisons of soil- and solution-grown plants are obviously limited, in this experiment, to wheat, barley, beans, and sunflowers. In the solution the sunflowers contained about 2.8 times as much calcium as the wheat, whereas, in the soil, they contained about 3.7 times as much. Similarly, if potassium percentages are compared the greatest difference is found between beans and barley. In the solution the barley contained about 1.7 times as much potassium as the beans, whereas in the soil it contained about 3.4 times as much. Comparisons of the other percentage figures in table 1 reveal the fact that in the cases of magnesium, nitrogen, and phosphorus, also, the variability was not so great when the plants were grown together in the culture solution as when grown together in the loam soil.

In addition to the fact that absorption from the culture solution was greater

Fig. 1-A Composition Of Plants Grown Together in loam Soil

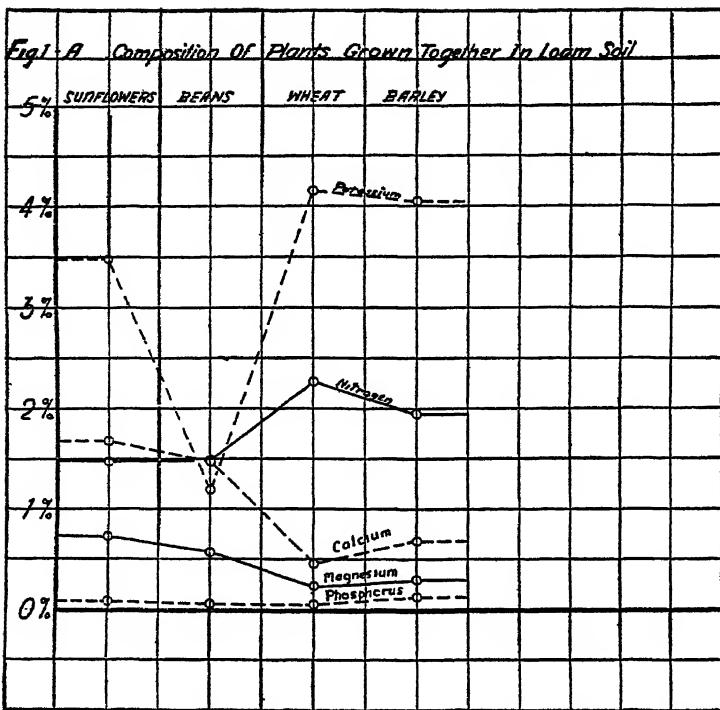
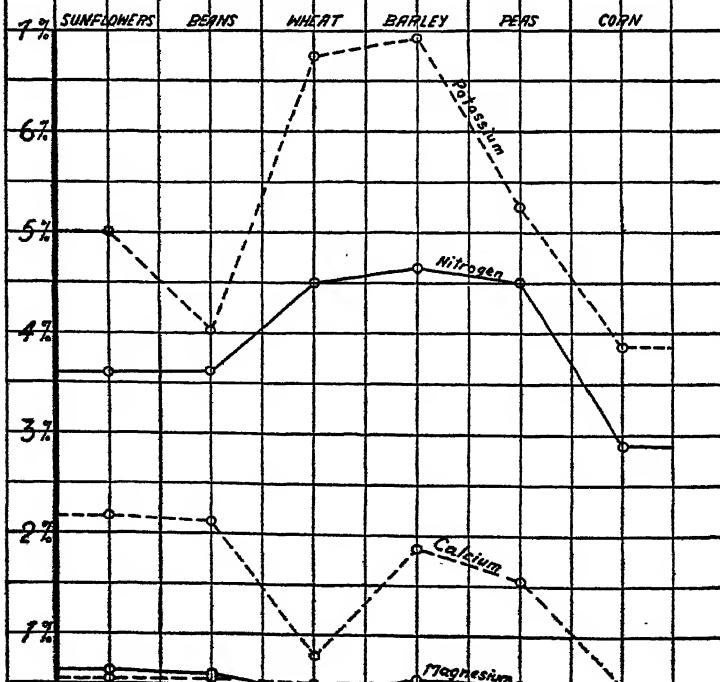


Fig. 1-B Composition Of Plants Grown Together In Culture Solution



than from the loam soil, and that there was less variability in absorption from the solution than from the soil, it will be observed that there are certain characteristic differences in absorption of inorganic elements by various crop plants apparent in both culture solution and soil-grown plants. It will be observed that there is a certain similarity in the composition graphs for both culture solution and soil (fig. 1).

The calcium percentages of sunflowers and beans grown in culture solution are relatively high, and are followed by barley and peas; whereas wheat and corn are relatively low in calcium. In the cases of the four crops grown in loam soil, which can be compared directly with the culture solution crops, the same order of calcium content was obtained, but the differences between different crops were relatively greater.

The potassium percentages of barley and wheat grown in culture solution are relatively high, and are followed by peas and sunflowers, beans and corn. In the cases of the four crops grown in loam soil, the same order of potassium content was obtained, except that wheat was slightly higher in potassium than was barley, whereas in the solution barley was slightly higher than wheat.

The nitrogen percentages of barley, peas, and wheat grown in culture solution are almost alike, and are followed by beans and sunflowers, corn being lowest in this element. In the soil, wheat is higher in nitrogen than barley, and, as in the culture solution, beans and sunflowers are appreciably lower.

In the culture solution, the magnesium percentages of the different crops varied less than the percentages of any other element. Sunflowers and beans are highest in magnesium, and are followed by barley and peas, wheat and corn. In the four soil-grown crops, the magnesium variability is much greater, but exactly the same order of magnesium content was obtained.

The phosphorus percentages are relatively low, especially in the soil-grown crops, and are rather variable. The phosphorus percentages of sunflowers, beans, and barley grown in culture solution are almost alike, and are followed, in descending order, by wheat, corn, and peas. In the soil-grown crops, the order is quite different; barley is highest in phosphorus and is followed by sunflowers, wheat, and beans, in descending order. The supply of this element in the loam soil was evidently quite limited, however, as the quantities absorbed were very small; and since in all other cases the order of absorption from loam soil agrees fairly well with the order of absorption from the culture solution, it seems doubtful if the absorption of phosphorus from the loam soil is really characteristic of the different plant species.

In experiments previously reported (3), comparisons, at four different stages of growth, of percentage composition and of ratios in which ion equivalents were absorbed, brought out no evidence of large or characteristic differences in the types of absorption from a culture solution by barley and peas. This conclusion is borne out by the experiments described in this paper, except that the phosphorus content of peas was considerably smaller than

obtained in the experiments previously reported. There is some evidence in both sets of experiments that the phosphorus absorption of peas is smaller than that of barley.

Evidence from experiments previously reported (3) indicated that there is a characteristic difference in the type of absorption by barley and beans in the early stages at least. Beans absorbed more calcium, in proportion to potassium, from a given culture solution, than either barley or peas. This is also true of the experiments described in this paper, and confirms the previous results.

These rather carefully controlled experiments, and those previously reported, bring out certain differences and similarities in absorption which are evidently characteristic of the plant species studied. Sunflowers seem to be characteristically rich in calcium and magnesium, and moderately rich in potassium and phosphorus. Beans, also, seem to be characteristically rich in calcium and magnesium, and moderately rich in phosphorus, but rather poor in potassium. Peas, barley, and wheat resemble one another in type of absorption of inorganic elements, although wheat evidently absorbs less calcium than barley or peas. And, lastly, corn is distinctly low in the several inorganic elements absorbed from the culture solution, as compared to the other crops studied.

In the experiments reported in this paper the plants were harvested for analysis after they had made a strong vegetative growth and before any fruit had formed, as it was considered that this was, perhaps, the best single stage at which to compare their absorption. Of course it would be desirable to analyze the plants at other stages, and in the previously reported experiments with barley and peas the plants were analyzed at four different stages of growth.

Tables of plant analyses may be obtained from different sources, but the analyses figures from various sources differ greatly, and it is evident from the experiments reported in this paper that the character of the soil and other factors greatly influence the character of the absorption. Evidently the best way of determining the selective action of different plant species is to measure their absorption when grown in a uniform environment. By growing the plants together in a culture solution, free from solid particles, a very important environmental factor may be controlled more easily, apparently, than in any other manner.

SUMMARY

Carefully controlled water culture experiments, supplemented by soil culture experiments, bring out certain differences and similarities in absorption of inorganic elements which are evidently characteristic of the six plant species studied.

Generally speaking, absorption from the culture solution was greater than

from the loam soil, and there was much less variability in absorption from the solution than from the soil.

Sunflowers (*Helianthus annuus*) are evidently characteristically rich in calcium and magnesium, and moderately rich in potassium and phosphorus.

Beans (*Phaseolus vulgaris*) are rich in calcium and magnesium, and moderately rich in phosphorus, but rather poor in potassium.

Peas (*Pisum sativum*), barley (*Hordeum sativum*), and wheat (*Triticum vulgare*) resemble one another in type of absorption of inorganic elements, although wheat evidently absorbs less calcium than barley or peas.

Corn (*Zea mays*) is distinctly low in the several inorganic elements absorbed from the culture solution, as compared to the other crops studied.

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OXIDATION OF SULFUR IN LIMED AND UNLIMED SOILS¹

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OBJECT OF THE INVESTIGATION

In a previous investigation (3) of the effects of sulfur oxidation in Kentucky soils on the solubility of the potassium, the writer found that in six of the seven soils compared, more sulfur was oxidized in the limed soil than in the corresponding unlimed sample. Since only seven soils were used in the earlier work, it was considered desirable in this investigation to verify the former results on a larger number of samples taken from the principal soil areas of Kentucky.

A more extended investigation of this nature would incidentally show whether Kentucky soils have the capacity to oxidize the necessary quantity of sulfur, in a period of time not exceeding the growing season; to supply the sulfur requirements of crops.

EXPERIMENTAL

The samples used in the work were all cultivated surface soils collected to a depth not exceeding 6 inches, and at least one was taken from each of the eleven principal soil areas of Kentucky. Arranged in the order of relative size beginning with the largest, the areas are as follows:

Eastern Coal Field Area

<i>Soil Number</i>	
86669	Harlan County. Light brown silty clay loam containing considerable gravel.
86672	Morgan County. Yellowish silty clay loam.
86676	Owsley County. Very light reddish-brown silty clay loam containing considerable gravel.
86769	Breathitt County. Light grayish-brown silty clay loam containing considerable gravel.

Cincinnati Area

86671	Franklin County. Yellowish-brown silty clay loam (Eden clay loam of the Bureau of Soils).
86674	Kenton County. Light brown silty clay loam.

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² The author desires to express his thanks to Dr. J. S. McHargue, acting head, and to Dr. A. M. Peter, of the department of chemistry, for helpful criticism in the preparation of the manuscript; also to the county agents and others in the collection of the samples.

86675 Henry County. Light brown silty clay loam.
 86681 Spencer County. Yellowish-brown silty clay loam.
 86683 Campbell County. Yellowish-brown silty clay loam.
 86689 Bracken County. Light brown silty clay loam.
 86690 Mason County. Light brown silty clay loam (Hagerstown loam of the Bureau of Soils).

St. Louis Area

86666 Logan County. Reddish-brown silty clay loam (Decatur clay loam of the Bureau of Soils).
 86685 Hardin County. Very light reddish-brown silty clay loam.

Western Coal Field Area

86668 McLean County. Very light brown silty clay loam.
 86678 Hancock County. Very light brown silty clay loam.

Waverly Area

86686 Hardin County. Very light reddish-brown silty clay loam.
 86688 Adair County. Very light brown silty clay loam containing considerable gravel.

Quaternary Area

86680 Graves County. Very light brown silt loam.
 86684 Graves County. Light reddish-brown silt loam.

Chester Area

86718 Caldwell County. Very light brown silty clay loam.

Trenton Area

86670 Jessamine County. Very light reddish-brown silt loam containing considerable gravel and some fragments of limestone (Hagerstown silt loam of the Bureau of Soils).
 86677 Franklin County. Very light reddish-brown silt loam (Hagerstown silt loam of the Bureau of Soils).
 86687 Mercer County. Light reddish-brown silt loam.

Alluvial Area

86705 Oldham County. Light brown silty clay loam.
 86717 Hancock County. Light brown silty clay loam.

Devonian Area

86667 Bath County. Brownish silty clay loam.
 86754 Jefferson County. Grayish silty clay loam.

Silurian Area

86673 Oldham County. Light brown silty clay loam.
 86697 Trimble County. Brown silty clay loam.
 86747 Bath County. Red-brown silty clay loam.
 86755 Jefferson County. Very light reddish-brown silty clay loam.

The samples from each area are representative of large tracts of land. The most fertile areas are the Alluvial and Trenton and the poorest are the Waverly and Chester.

The samples were collected in the fall of 1926, immediately air-dried and put through a 2-mm. sieve for the experiments. The quantities of sulfur (flowers) and calcium carbonate added were, respectively, 250 p.p.m. and 4000 p.p.m. of the air-dried soil. The sulfur and calcium carbonate were of the best C.P. grade and were previously tested to insure the absence of sulfide and sulfate. Nothing was added other than these chemicals and the required amount of each was intimately mixed with the air-dried sample, after which distilled water was added to the extent of 15 per cent of the weight of the air-dried soil. The moist samples were in good physical condition and could be stirred without packing.

The experiments were carried on in pint glass jars which had been previously weighed and were kept covered with watch-glasses. At intervals of one week during the first 30 days and of one month during the last 90 days, the necessary amount of distilled water was added to replace the small amount lost by evaporation. Each time this was done, the soil was thoroughly stirred.

The soils were kept in the jars at room temperature for 4 months. After 30 days and again after 120 days, portions were weighed and without being air-dried were used in the hydrochloric acid digestion for the determination of sulfate. Previous to the weighings, the required amount of distilled water was added to restore the moisture content, after which the samples were thoroughly stirred. The amounts of water and of calcium carbonate present in the soils were taken into consideration in preparing the hydrochloric acid for the digestion so as not to affect its volume and strength.

Sulfate sulfur and hydrogen-ion concentration determinations were made on the original and on the treated soils. All pH, acidity, and alkalinity determinations were made on the air-dried samples, as was the sulfate sulfur in the original soil.

METHODS OF ANALYSIS

Sulfate sulfur. A quantity of the moist soil equivalent to 40 grams of the air-dried sample was digested with 800 cc. of 1 per cent hydrochloric acid for 24 hours, shaken thoroughly each hour during the 10-hour-day period. The solution was filtered until clear by pouring the filtrate on the soil mass contained in the filter. An aliquot representing 30 grams of the air-dried soil was evaporated to dryness; 5 cc. of 19 per cent hydrochloric acid and then distilled water were added to the residue. The solution was heated on the steam bath, then filtered and the filtrate of about 100 cc. was heated to boiling and an excess of a hot 10 per cent solution of barium chloride was slowly added with shaking. The solution was then heated for an hour or so on the steam bath and after standing overnight, the barium sulfate was filtered, washed, and determined in the usual manner. After the

TABLE 1
Sulfate sulfur in soils, air-dry basis

SOIL NUMBER	ORIGINAL AIR-DRIED SOIL	MOIST SOIL AFTER 30 DAYS' INCUBATION								
		No treatment	S treatment	Proportion of added S oxidized without CaCO ₃ *		CaCO ₃ treatment	CaCO ₃ + S treat- ment		Proportion of added S oxidized with CaCO ₃ †	
		S	S	S	S	S	S	S	S	
		p.p.m.	p.p.m.	p.p.m.	per cent	p.p.m.	p.p.m.	p.p.m.	per cent	
<i>Eastern Coal Field Area</i>										
86669	14	12	63	51	20.4	12	55	43	17.2	
86672	91	97	119	22	8.8	102	117	15	6.0	
86676	13	6	43	37	14.8	13	45	32	12.8	
86769	9	7	57	50	20.0	4	62	58	23.2	
Average	32	31	71	40	16.0	33	70	37	14.8	
<i>Cincinnati Area</i>										
86671	5	12	42	30	12.0	13	51	38	15.2	
86674	9	13	66	53	21.2	11	60	49	19.6	
86675	16	15	64	49	19.6	11	64	53	21.2	
86681	21	8	43	35	14.0	13	41	28	11.2	
86683	26	15	57	42	16.8	12	55	43	17.2	
86689	7	7	48	41	16.4	12	49	37	14.8	
86690	9	15	59	44	17.6	19	52	33	13.2	
Average	13	12	54	42	16.8	13	53	40	16.0	
<i>St. Louis Area</i>										
86666	15	14	65	51	20.4	11	48	37	14.8	
86685	57	49	132	83	33.2	62	122	60	24.0	
Average	36	32	99	67	26.8	37	85	48	19.2	
<i>Western Coal Field Area</i>										
86668	56	44	122	78	31.2	43	104	61	24.4	
86678	11	14	99	85	34.0	30	87	57	22.8	
Average	34	29	111	82	32.8	37	96	59	23.6	
<i>Waverly Area</i>										
86686	11	9	72	63	25.2	11	64	53	21.2	
86688	3	6	53	47	18.8	7	52	45	18.0	
Average	7	8	63	55	22.0	9	58	49	19.6	

TABLE 1—Concluded

SOIL NUMBER	ORIGINAL AIR-DRIED SOIL	MOIST SOIL AFTER 30 DAYS' INCUBATION								
		No treatment	S treatment	Proportion of added S oxidized without CaCO ₃ *		CaCO ₃ treatment	CaCO ₃ + S treatment		Proportion of added S oxidized with CaCO ₃ †	
		S	S	S	S	S	S	S	S	
		p.p.m.	p.p.m.	p.p.m.	per cent	p.p.m.	p.p.m.	p.p.m.	per cent	
<i>Quaternary Area</i>										
86680	33	33	123	90	36.0	34	127	93	37.2	
86684	17	7	43	36	14.4	5	51	46	18.4	
Average	25	20	83	63	25.2	20	89	69	27.6	
<i>Chester Area</i>										
86718	7	7	49	42	16.8	5	32	27	10.8	
<i>Trenton Area</i>										
86670	11	9	45	36	14.4	13	40	27	10.8	
86677	21	9	61	52	20.8	11	50	39	15.6	
86687	11	8	64	56	22.4	14	58	44	17.6	
Average	14	9	57	48	19.2	13	49	36	14.4	
<i>Alluvial Area</i>										
86705	11	11	62	51	20.4	11	48	37	14.8	
86717	19	18	76	58	23.2	20	77	57	22.8	
Average	15	15	69	54	21.6	16	63	47	18.8	
<i>Devonian Area</i>										
86667	21	20	67	47	18.8	21	73	52	20.8	
86754	14	18	69	51	20.4	16	73	57	22.8	
Average	18	19	68	49	19.6	19	73	54	21.6	
<i>Silurian Area</i>										
86673	19	19	79	60	24.0	25	66	41	16.4	
86697	12	8	44	36	14.4	11	45	34	13.6	
86747	5	9	45	36	14.4	10	49	39	15.6	
86755	10	10	60	50	20.0	10	50	40	16.0	
Average	12	12	57	45	18.0	14	53	39	15.6	
General average	19	17	67	50	20.0	19	63	44	17.6	

* 250 p.p.m. of S added. The figures under this heading were obtained by subtracting those given in the "No treatment" column from those given in the "S treatment" column.

† 250 p.p.m. of S added. The figures under this heading were obtained by subtracting those given in the "CaCO₃ treatment" column from those given in the "CaCO₃ + S" treatment column.

TABLE 2
Sulfate sulfur in soils, air-dry basis

SOIL NUMBER	ORIGINAL AIR-DRIED SOIL	MOIST SOIL AFTER 120 DAYS' INCUBATION								
		No treatment	S treatment	Proportion of added S oxidized without CaCO_3^*		CaCO ₃ treatment	CaCO ₃ + S treatment		Proportion of added S oxidized with CaCO_3^{\dagger}	
		S	S	S	S	S	S	S	S	
		p.p.m.	p.p.m.	p.p.m.	per cent	p.p.m.	p.p.m.	p.p.m.	per cent	
<i>Eastern Coal Field Area</i>										
86669	14	16	121	105	42.0	19	124	105	42.0	
86672	91	98	157	59	23.6	83	158	75	30.0	
86676	13	11	91	80	32.0	14	78	64	25.6	
86769	9	11	110	99	39.6	10	115	105	42.0	
Average	32	34	120	86	34.4	32	119	87	34.8	
<i>Cincinnati Area</i>										
86671	5	19	71	52	20.8	16	73	57	22.8	
86674	9	16	136	120	48.0	16	129	113	45.2	
86675	16	17	118	101	40.4	13	107	94	37.6	
86681	21	13	67	54	21.6	18	61	43	17.2	
86683	26	28	92	64	25.6	23	112	89	35.6	
86689	7	6	105	99	39.6	8	107	99	39.6	
86690	9	12	113	101	40.4	16	99	83	33.2	
Average	13	16	100	84	33.6	16	98	82	32.8	
<i>St. Louis Area</i>										
86666	15	30	184	154	61.6	18	156	138	55.2	
86685	57	59	203	144	57.6	62	205	143	57.2	
Average	36	45	194	149	59.6	40	181	141	56.4	
<i>Western Coal Field Area</i>										
86668	56	49	192	143	57.2	50	209	159	63.6	
86678	11	34	166	132	52.8	24	159	135	54.0	
Average	34	42	179	137	54.8	37	184	147	58.8	
<i>Waverly Area</i>										
86686	11	15	139	124	49.6	13	138	125	50.0	
86688	3	8	107	99	39.6	11	116	105	42.0	
Average	7	12	123	111	44.4	12	127	115	46.0	

TABLE 2—*Concluded*

SOIL NUMBER	ORIGINAL AIR-DRIED SOIL	MOIST SOIL AFTER 120 DAYS' INCUBATION								
		No treatment	S treatment	Proportion of added S oxidized without CaCO ₃ *		CaCO ₃ treatment	CaCO ₃ + S treatment		Proportion of added S oxidized with CaCO ₃ †	
		S	S	S	S	S	S	S	S	
		p.p.m.	p.p.m.	p.p.m.	per cent	p.p.m.	p.p.m.	p.p.m.	per cent	
<i>Quaternary Area</i>										
86680	33	39	186	147	58.8	38	198	160	64.0	
86684	17	18	119	101	40.4	8	113	105	42.0	
Average	25	29	153	124	49.6	23	156	133	53.2	
<i>Chester Area</i>										
86718	7	12	121	109	43.6	12	123	111	44.4	
<i>Trenton Area</i>										
86670	11	18	99	81	32.4	18	104	86	34.4	
86677	21	16	110	94	37.6	15	98	83	33.2	
86687	11	27	120	93	37.2	16	98	82	32.8	
Average	14	20	110	90	36.0	16	100	84	33.6	
<i>Alluvial Area</i>										
86705	11	19	125	106	42.4	16	120	104	41.6	
86717	19	22	149	127	50.8	28	153	125	50.0	
Average	15	21	137	116	46.4	22	137	115	46.0	
<i>Devonian Area</i>										
86667	21	27	159	132	52.8	30	183	153	61.2	
86754	14	17	139	122	48.8	22	149	127	50.8	
Average	18	22	149	127	50.8	26	166	140	56.0	
<i>Silurian Area</i>										
86673	19	22	140	118	47.2	17	136	119	47.6	
86697	12	7	123	116	46.4	10	115	105	42.0	
86747	5	8	77	69	27.6	10	79	69	27.6	
86755	10	12	142	130	52.0	14	128	114	45.6	
Average	12	12	121	109	43.6	13	115	102	40.8	
General average	19	23	128	105	42.0	21	127	106	42.4	

* 250 p.p.m. of S added. The figures under this heading were obtained by subtracting those given in the "No treatment" column from those given in the "S treatment" column.

† 250 p.p.m. of S added. The figures under this heading were obtained by subtracting those given in the "CaCO₃ treatment" column from those given in the "CaCO₃ + S" treatment column.

TABLE 3
Hydrogen-ion concentration and acidity or alkalinity of soils, air-dry basis

SOIL NUMBER	ORIGINAL AIR-DRIED SOIL pH	MOIST SOIL AFTER 120 DAYS' INCUBATION											
		No treatment				S treatment				CaCO ₃ treatment		CaCO ₃ + S treatment	
		Titration		Titration		Titration		Titration		Titration		Titration	
		pH	Alkalinity as CaCO ₃	Acidity as H ₂ SO ₄	pH	Alkalinity as CaCO ₃	Acidity as H ₂ SO ₄	pH	Alkalinity as CaCO ₃	Acidity as H ₂ SO ₄	pH	Alkalinity as CaCO ₃	Acidity as H ₂ SO ₄
		p. p. m.	p. p. m.	p. p. m.	p. p. m.	p. p. m.	p. p. m.	p. p. m.	p. p. m.	p. p. m.	p. p. m.	p. p. m.	p. p. m.
<i>Eastern Coal Fields Area</i>													
86669	5.2	5.0	..	20	5.3	..	20	7.0	..	59	6.7	..	39
86672	5.2	5.2	70	..	5.0	90	..	7.0	16	..	7.0	20	..
86676	4.6	4.6	20	..	4.4	100	..	6.6	30	..	6.6	80	..
86769	6.6	6.5	20	..	6.4	30	..	7.0	..	39	6.8	..	20
Average	5.4	5.3	5.3	6.9	6.8
<i>Cincinnati Area</i>													
86671	5.6	5.4	..	39	5.4	..	39	6.8	..	39	6.8	..	47
86674	5.2	5.2	24	..	5.0	34	..	7.0	..	27	7.0	..	31
86675	5.0	5.0	20	..	5.2	60	..	7.0	..	16	6.8	..	39
86681	6.5	6.6	26	..	6.6	26	..	7.0	..	20	7.0	..	20
86683	6.2	6.2	34	..	6.2	30	..	7.0	40	..	7.0	40	..
86689	5.2	5.2	30	..	5.2	50	..	7.0	16	..	6.8	36	..
86690	5.0	4.6	40	..	4.4	70	..	6.8	..	39	6.6	16	..
Average	5.5	5.5	5.4	6.9	6.9
<i>St. Louis Area</i>													
86666	5.4	5.0	100	..	4.8	100	..	7.2	..	39	7.0	10	..
86685	4.8	4.6	34	..	4.6	44	..	7.0	44	..	6.8	40	..
Average	5.1	4.8	67	..	4.7	72	..	7.1	6.9	25	..
<i>Western Coal Fields Area</i>													
86668	5.0	4.6	50	..	4.6	90	..	7.0	56	..	6.8	40	..
86678	6.6	6.5	36	..	6.1	50	..	7.2	6	..	7.2	6	..
Average	5.8	5.6	43	..	5.4	70	..	7.1	31	..	7.0	23	..
<i>Waverly Area</i>													
86686	5.0	4.8	36	..	4.6	46	..	7.2	..	24	7.2	..	12
86688	5.4	5.0	30	..	4.6	30	..	7.2	..	39	7.2	..	59
Average	5.2	4.9	33	..	4.6	38	..	7.2	..	32	7.2	..	36

TABLE 3—Continued

SOIL NUMBER	ORIGINAL AIR-DRIED SOIL pH	MOIST SOIL AFTER 120 DAYS' INCUBATION														
		No treatment				S treatment				CaCO ₃ treatment			CaCO ₃ + S treatment			
		pH	Titration		pH	Titration		pH	Titration		pH	Titration		pH	Titration	
			Alkalinity as CaCO ₃	Acidity as H ₂ SO ₄		Alkalinity as CaCO ₃	Acidity as H ₂ SO ₄		Alkalinity as CaCO ₃	Acidity as H ₂ SO ₄		Alkalinity as CaCO ₃	Acidity as H ₂ SO ₄		p. p. m.	p. p. m.
<i>Quaternary Area</i>																
86680	5.1	4.8	32	..	5.0	52	..	7.2	..	16	7.2	10	..			
86684	5.2	5.0	24	..	4.8	30	..	7.2	26	..	7.0	30	..			
Average	5.2	4.9	28	..	4.9	41	..	7.2	7.1	20	..			
<i>Chester Area</i>																
86718	5.4	5.0	40	..	4.8	44	..	7.0	..	59	7.0	..	24			
<i>Trenton Area</i>																
86670	5.4	5.4	..	39	5.6	..	35	7.0	..	39	6.8	..	51			
86677	4.7	4.6	30	..	4.6	40	..	6.8	10	..	6.8	30	..			
86687	5.0	4.8	40	..	4.6	60	..	6.6	20	..	6.6	40	..			
Average	5.0	4.9	4.9	6.8	6.7			
<i>Alluvial Area</i>																
86705	7.0	6.8	20	..	6.8	16	..	7.0	..	31	7.0	..	39			
86717	7.0	7.2	..	20	7.0	16	..	7.0	..	98	7.2	..	20			
Average	7.0	7.0	6.9	16	..	7.0	..	65	7.1	..	30			
<i>Devonian Area</i>																
86667	5.0	4.8	80	..	4.9	170	..	6.8	30	..	6.2	60	..			
86754	5.4	5.4	36	..	5.0	30	..	7.4	..	78	7.2	..	20			
Average	5.2	5.1	58	..	5.0	100	..	7.1	6.7			
<i>Silurian Area</i>																
86673	5.0	5.2	20	..	5.0	30	..	7.0	..	20	7.0	..	20			
86697	5.2	5.0	30	..	4.8	70	..	7.0	..	39	7.0	..	31			
86747	5.2	4.6	24	..	5.1	70	..	6.8	30	..	6.6	6.6	..			
86755	5.2	4.8	24	..	4.8	50	..	7.0	..	47	6.8	..	20			
Average	5.2	4.9	25	..	4.9	55	..	7.0	6.9			
General average	5.4	5.3	5.2	7.0	6.9			

precipitate was weighed, it was treated with concentrated sulfuric acid and concentrated hydrofluoric acid, to eliminate traces of silica if present, and was reweighed.

Acidity and alkalinity. Ten grams of the air-dried soil was digested for 30 minutes with 80 cc. of hot distilled water, shaken every 5 minutes, after which it was cooled, made to 100 cc. volume, filtered until clear, and an aliquot equivalent to 5 grams of the air-dried soil was taken for the titration. The solution was boiled to expel carbon dioxide and afterwards titrated with 0.02 *N* sodium hydroxide or 0.02 *N* hydrochloric acid, using phenolphthalein as the indicator. When an alkaline solution was titrated the equivalence is doubled, on the theory that the substance titrated was a carbonate. For acid solutions, the actual equivalence in sulfuric acid is stated.

TABLE 4
Effect of stirring on sulfate sulfur obtained in the treated soils, air-dry basis, after 30 days' incubation

TREATMENT	STIRRED EACH DAY				STIRRED EACH WEEK			
	86754		86755		86754		86755	
	S	Per cent of added S oxidized	S	Per cent of added S oxidized	S	Per cent of added S oxidized	S	Per cent of added S oxidized
	p. p. m.		p. p. m.		p. p. m.		p. p. m.	
None.....	13	8	18	10
S.....	68	73	69	60
	55	22.1	65	26.0	51	20.4	50	20.0
CaCO ₃	16	12	16	10
CaCO ₃ + S.....	84	67	73	50
	68	27.2	55	22.0	57	22.8	40	16.0

Hydrogen-ion concentration. The colorimetric method employed by the writer in the previous investigation was used. The indicators were those recommended by Clark and Lubs (1, p. 66). The procedure was to moisten 0.2 gram of the air-dried soil on a porcelain plate with a few drops of aqueous indicator, sufficient being added so that the soil was saturated and the liquid had a tendency to drain from the soil when the plate was inclined. After 1 minute, the liquid was drawn away from the soil with a platinum wire, spread, and the color compared with the Clark and Lubs standard color chart (1, p. 41). The soil for this work was put through a 2 mm. sieve and not ground fine because it was thought that grinding might affect the pH determination.

The sulfate sulfur determinations after 30 days' and 120 days' incubation are given in tables 1 and 2. The pH, acidity, and alkalinity determinations are given in table 3.

SUMMARY

This investigation consists of a study of the oxidation of sulfur both in the presence and absence of calcium carbonate when added to 31 surface soils from the principal soil areas of Kentucky.

A former investigation showed that in 7 samples tested, 6 limed soils oxidized more sulfur than the corresponding unlimed samples. The present work in which 31 samples were used was undertaken to confirm more generally if possible, the earlier results, although some details differed in the two investigations.

Every soil oxidized appreciable quantities of the added sulfur, with or without calcium carbonate, in 30 days and still larger quantities after 120 days, which was the duration of the experiment. The quantity of sulfur added was 250 p.p.m. of the air-dried soil and the amount of the added sulfur which was oxidized after 30 days in the unlimed soil varied from 8.8 to 36 per cent, whereas in the limed soil it varied from 6 to 37.2 per cent. After 120 days, the amount varied from 20.8 to 61.6 per cent in the unlimed soils and from 17.2 to 64 per cent in the limed samples. The differences between the above maximum and minimum ranges in the limed and unlimed samples for the same period of time are not significant.

According to the sulfur requirements of farm crops as given by Hart and Peterson (2), sufficient quantities of the added sulfur were oxidized in every soil even after 30 days to supply the sulfur requirements of almost any crop under maximum production even though the sulfur normally present in the soil and rain is not considered. The minimum amount of sulfur oxidized in 30 days was 30 pounds per acre, which may be taken as equivalent to 15 p.p.m. in comparison with the figures, as shown in table 1. Hart and Peterson found that an average crop of alfalfa, which is one of the few crops containing large amounts of sulfur, removes 26 pounds per acre of sulfur from the soil. Only two crops; namely, cabbage and turnips, which remove 39.2 and 37 pounds per acre of sulfur, respectively, from the soil, exceed alfalfa.

Regardless of the percentage increase, the sulfate in 8 of the moist untreated samples after 30 days was greater than in the original, equal in 6, and less in the remaining 17. After 120 days, however, it was larger in 25 of the samples and less in the remaining 6 than in the original. This fact, considered in connection with the general average, indicates a gradual oxidation to sulfate to the sulfur originally present in other combinations in these soils when they were kept moist at ordinary temperature. Again, on comparing the limed and unlimed moist soils to which no sulfur was added, it will be found that after 30 days, 19 of the limed samples contain more, 3 have the same amount, and 9 have less sulfate than the corresponding unlimed soils. After 120 days, only 14 of the limed samples have a larger amount, 3 have the same, and 14 a smaller amount of sulfate than the unlimed. The final results show that where no sulfur was added, calcium carbonate has had little influence on the oxidation to sulfate of the combined sulfur in the soil.

Very little consistent relation was found between the hydrogen-ion concentrations of the treated soils, either in their initial or final pH values, and their acidity or alkalinity by titration or the amounts of added sulfur oxidized by them. The amounts of acid found in the samples by the titrations were usually not in proportion to the quantities of sulfur oxidized by them. The soils treated with calcium carbonate were nearly all rendered neutral or nearly neutral. The averages show that the soil that had been kept moist for 120 days had a slightly lower pH value than the original, and the soils, either limed or unlimed, to which sulfur was added also had a slightly lower average pH value than the corresponding samples without sulfur.

A comparison of the sulfur treatments with and without calcium carbonate shows that after 30 days only 9 gave increases in sulfate when calcium carbonate was present whereas the remaining 22 showed losses. After 120 days, however, 15 limed samples showed gains, 3 were equal, and 13 were less. According to the amount of the added sulfur which was oxidized, this shows that the number of limed soils which showed gains over the unlimed, increased after a larger period of incubation. The general averages for the longer period of time show, however, that about the same percentage of the added sulfur was oxidized by the two groups of soils.

If a comparison of the amounts of sulfur oxidized after 30 days and 120 days in the limed and unlimed soils is made, it appears that a mixture of at least two groups of the sulfur-oxidizing bacteria may have had a part in the reaction.

Probably one group was predominant at the end of the 30-day period, possibly because the calcium carbonate had not sufficiently reacted with the soil materially to accelerate the growth of the other group. Between the 30-day and 120-day periods, however, the calcium carbonate had more time to act on the soil thus making the conditions more favorable for a different group of bacteria to take part, with a consequent increase in the relative amounts of sulfur oxidized. According to the behavior of many of the soils, it is possible that a mixture of two sulforying organisms described by Waksman (4) were present in these soils. At least the conditions he mentions which are favorable for the presence of the two organisms parallel those found in these experiments. It is doubtful if many *Thiobacillus thiooxidans* were present, however, because Waksman states that they will not thrive in a medium with a pH value very much above 4.0, and the lowest pH value of any of the treated soils was 4.4.

The treated soils in this work were maintained at a lower moisture content and were not stirred as frequently as the ones in the earlier investigation. Moreover, the average room temperature was not so high, particularly at night, in these experiments, for they were carried on during the winter months whereas the earlier experiments were made in the summer. Elevated temperature is probably one factor which promotes sulfification as well as nitrification.

The writer is of the opinion that thorough aeration is another important factor in the oxidation of sulfur by soils and if the samples had been more

frequently stirred, still larger quantities of sulfur might have been oxidized in the same time. To demonstrate this, duplicate experiments were made on two of the samples, 86754 and 86755, by incubating them for 30 days under the same conditions except that they were stirred each day instead of each week as before. The comparative results obtained on these samples are given in table 4. According to the results obtained on these two samples, it is probable that if all the treated soils had been more thoroughly aerated, particularly at a higher temperature and for a longer period of time, a larger number of the limed samples would have oxidized greater quantities of sulfur than the unlimed.

The results obtained in this work would be of practical value provided it should ever become necessary to add sulfur to Kentucky soils in order to supply this essential of plant-food inasmuch as the necessary quantities of sulfur could be very readily oxidized and any deleterious acid effect prevented by the simultaneous addition of limestone.

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THE APPLICATION OF THE ANTIMONY ELECTRODE TO THE DETERMINATION OF THE pH VALUES OF SOILS

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The antimony electrode was employed by Uhl and Kestranek (4) for analytical neutralizations and later an extensive study of its properties was made by Kolthoff and Hartong (2). More recently Franke and Willaman (1) have made a study of the antimony electrode and its application to the determination of the hydrogen-ion exponents of paper-mill liquors. Since the use of this electrode dispenses with the necessity of plating electrodes and the use of hydrogen, quinhydrone, etc., it tends to simplify and expedite the determination as compared to the customary electrometric procedures.

The present work was therefore undertaken to determine the applicability of the antimony electrode to the determination of the hydrogen-ion exponents of soil suspensions.

THEORETICAL CONSIDERATIONS

The equations given by Kolthoff and Hartong (2) for measurements against the *N* calomel electrode at 14.0°C. are as follows:

$$(A) \quad E = 0.0415 + 0.0485 \text{ pH} \text{ (from pH 1 to 5)}$$
$$(B) \quad E = 0.009 + 0.0536 \text{ pH} \text{ (pH above 9)}$$

The equation given by Franke and Willaman (1) for potentials measured against the *N* calomel electrode is as follows:

$$(C) \quad E = 0.050 + 0.054 \text{ pH, at } 25.0^\circ\text{C.}$$

The antimony electrode results given in the subsequent tables were computed from equation (C) for 25.0°C., the determinations being made in a room especially adapted to potentiometric work and kept at approximately 25.0°C. during the course of the determinations. All recorded potentials were measured against the saturated calomel electrode and converted to the *N* calomel electrode by adding the difference, 0.0384 volts at 25.0°C. The pH values are given to the second decimal place merely for purposes of comparison.

EXPERIMENTAL

Electrodes

Kolthoff and Hartong (2) used for their electrode, Kahlbaum antimony analyzing 99.97 per cent antimony, which was melted and poured into a rod-

¹ Soil Fertility Investigations.

like mold. Kolthoff and Hartong (2) obtained more reliable results and constant potentials more rapidly when a little antimony trioxide was added; however, according to Uhl and Kestranek (4), whose results Kolthoff and Hartong also confirmed, the antimony contains sufficient antimony oxide so that it may be used without any further addition. Franke and Willaman (1) state that after an extensive series of trials with various types of antimony electrodes the ordinary pure stick antimony was found to be the best. The best castings were obtained by pouring the molten antimony into a pyrex tube sealed at one end and imbedded in a heated sand bath. For the determination of the hydrogen-ion exponents of soils the writer has used stick antimony purchased as C. P. and measuring about 7 mm. in diameter and cut into 4 cm. lengths. Many electrodes were used as such and also recast from this antimony, while a number of electrodes were also cast from a sample of antimony obtained from the U. S. Bureau of Standards. This antimony analyzed Sb, 99.94 per cent; Pb, 0.05 per cent; Fe, 0.013 per cent; Cu, none; Sn, none; Zn, none; and As, a trace.

Some electrodes were made by melting the antimony in a pyrex tube sealed at one end and gradually cooled, whereas others were made by pouring the molten metal into the pyrex tube imbedded in a heated sand bath, thus permitting gradual cooling. In most instances the electrodes were of varying size and were filed fairly smooth and then polished on a buffering wheel. The electrodes took on a very bright finish but gradually oxidized in the air. In this respect Franke and Willaman (1) state that a bright electrode no doubt gives a quicker response than a tarnished one but shows more tendency for a potential drift, and consequently they recommend a tarnished electrode. The electrodes tarnish so readily that it would require frequent polishing to offset this. Connection was made to the electrodes by soldering them to a copper wire. The electrodes were then held securely in place in a pyrex tube with sealing wax after a shoulder had been ground on the electrode so that it fit the tube snugly.

Procedure

Fifteen grams of air-dried soil and 30 cc. of water were shaken in a pyrex test tube for approximately 1 minute. This suspension was allowed to stand a short time for sedimentation. A portion of the supernatant liquid, sufficient to fill the neck of the vessel and the bore of the stopcock, was poured into the vessel previously described (3). The end of the vessel is filled with saturated potassium chloride solution and the vessel is attached to a shaker and connected with the saturated calomel electrode. The remainder of the soil suspension was poured into the vessel, and the plain antimony electrode was well washed with distilled water, inserted in a rubber stopper, and placed in the vessel. The vessel was shaken about 1 or 2 minutes and the potential read during shaking. In most instances the potential that was read with the vessel at rest drifted rapidly.

TABLE I
Variation of antimony electrode measurements with time

SOIL TYPE	ELECTRODE VESSEL SHAKING						ELECTRODE VESSEL AT REST
	1 minute	3 minutes	5 minutes	10 minutes	15 minutes	5 minutes	
watts	pH	watts	pH	watts	pH	watts	pH
Norfolk fine sandy loam, Norfolk, Va.	{ 0.2658 4.71	0.2658 4.71	0.2658 4.71	0.2658 4.71	0.2658 4.71	0.2658 4.71	0.2662 4.71
{ 0.2657 4.71	0.2657 4.71	0.2657 4.71	0.2657 4.71	0.2656 4.70	0.2656 4.70	0.2668 4.73	
Portsmouth fine sandy loam, New Bern, N. C.	{ 0.3236 5.78	0.3224 5.76	0.3224 5.76	0.3218 5.74	0.3217 5.74	0.3267 5.84	
{ 0.3212 5.73	0.3210 5.73	0.3206 5.73	0.3208 5.73	0.3207 5.73	0.3234 5.77		
Hagerstown clay loam, State College, Pa.	{ 0.3885 6.98	0.3883 6.98	0.3881 6.97	0.3876 6.96	0.3877 6.96	0.4142 7.46	
{ 0.3853 6.92	0.3854 6.92	0.3858 6.93	0.3854 6.92	0.3850 6.91	0.3850 6.91	0.4140 7.45	
Hagerstown clay loam, State College, Pa.	{ 0.3940 7.08	0.3949 7.10	0.3944 7.09	0.3926 7.06	0.3922 7.05	0.4242 7.64	
{ 0.3933 7.07	0.3940 7.08	0.3950 7.10	0.3947 7.09	0.3950 7.10	0.4249 7.65		
Powers clay loam, Wiley, Colo.	{ 0.4165 7.50	0.4164 7.50	0.4162 7.49	0.4167 7.50	0.4174 7.51	0.4476 8.07	
{ 0.4168 7.50	0.4164 7.50	0.4164 7.50	0.4165 7.50	0.4167 7.50	0.4518 8.15		
Stockton clay adobe, Butte Co., Calif.	{ 0.4526 8.11	0.4510 8.14	0.4513 8.14	0.4500 8.12	0.4457 8.04	0.4879 8.82	
{ 0.4553 8.22	0.4548 8.21	0.4552 8.22	0.4546 8.20	0.4555 8.22	0.4958 9.97		
Fort Lyon clay loam, Las Animas, Colo.	{ 0.4388 7.91	0.4372 7.88	0.4370 7.88	0.4359 7.86	0.4356 7.85	
{ 0.4388 7.91	0.4383 7.90	0.4379 7.90	0.4376 7.90	0.4373 7.88		
Fallon loam, Churchill Co., Nev.	{ 0.5102 9.23	0.5076 9.18	0.5066 9.15	0.5066 9.15	0.5063 9.16	0.5196 9.41	
{ 0.5114 9.25	0.5107 9.24	0.5106 9.24	0.5098 9.23	0.5099 9.23	0.5304 9.61		

Kolthoff and Hartong (2) state that in order to obtain reliable results the liquid must be stirred during the determination, this being accomplished by a stirrer or the passage of an indifferent gas, such as hydrogen or nitrogen, through the solution. Uhl and Kestranek (4) state that the chief reason for the deviation from the correct titration results was due to the influence of the carbon dioxide of the air, and consequently they used carbon-dioxide-free air for agitation. Franke and Willaman (1) conclude that both oxygen and carbon dioxide can affect the potential, but that the magnitude of the effect is small, unless these gases are actually bubbled through the solution. The vessel used by the writer (3) is a closed type of shaking electrode, which prevents any undue contact of the soil suspension with the atmosphere.

Variation of antimony electrode measurements with time

In order to determine the constancy of potential of the antimony electrode, measurements were made on suspensions of duplicate samples of different soil types. These potential measurements, shown in table 1, were made after the indicated periods, during and after shaking of the electrode vessel.

TABLE 2
Comparison of pH results on soils by the antimony and hydrogen electrodes

ELECTRODE	pH VALUES												
Antimony.....	3.73	4.71	5.29	5.65	5.74	6.17	6.98	7.08	7.30	7.50	8.20	7.91	9.24
Hydrogen.....	3.62	4.76	5.34	5.51	5.68	6.04	7.07	7.28	7.43	7.70	7.91	7.97	9.17

The reproducibility and constancy of measurements may be considered very good for soils. It is quite apparent, however, that the potentials should be read during agitation. This conclusion seems to be in accord with that of previous investigators. In the case of one alkaline soil (Stockton clay adobe), the reproducibility as well as the constancy was somewhat erratic. The anomalous behavior of this soil was observed in a previous investigation (3) particularly with the quinhydrone electrode. As shown in table 1, equilibrium is generally reached in about 1 minute. Constant potentials were generally obtained by Uhl and Kestranek (4) in about 30 seconds, whereas Kolthoff and Hartong (2) and Franke and Willaman (1) obtained constant potentials within about 2 minutes.

COMPARISON OF RESULTS

Some promising preliminary results by way of comparison between the antimony and hydrogen electrodes are shown in table 2.

The agreement between the two electrodes, as shown in table 2, may be considered very good for the soils investigated. There is sufficient evidence to indicate that the purity and the crystallization of the antimony are factors

contributory in part at least to the constancy and reproducibility of the potentials.

Further work will be necessary to determine the applicability of the antimony electrode to the determination of the hydrogen-ion exponents of soils in general. It is to be hoped that the working out of these details will add another electrode useful in the determination of the hydrogen-ion exponents of soils and prove of further value in instances where the other methods cannot be used, particularly by virtue of its rapidity and simplicity.

SUMMARY

Results obtained with the antimony and hydrogen electrodes show very good agreement on the soils investigated, the soils ranging in pH values from about 3.6 to 9.2.

Constant and reproducible potentials were generally obtained in about 1 minute.

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CONTRIBUTION TO THE CHEMICAL COMPOSITION OF PEAT:

I. CHEMICAL NATURE OF ORGANIC COMPLEXES IN PEAT AND METHODS OF ANALYSIS

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The term "peat" may be used to designate an accumulation of organic matter which forms one or more horizons on the surface of the earth, as a result of the incomplete disintegration of plant and animal residues, under the influence of specific conditions, especially in the presence of an abundant supply of water. Known under different names in different countries, peat has attracted considerable attention both from the agriculturist and from the chemist, due to its wide occurrence, high content of organic matter and nitrogen, and, therefore, its utilization for the growth of agricultural crops and for the preparation of fertilizers and as a source of fuel.

Notwithstanding numerous contributions on the geological nature and botanical composition, origin, and practical utilization of peat, its chemistry is still comparatively little understood; this is especially true of the organic complexes which make up 50 to 99 per cent of the dry material of peat. Chemical analyses have been limited, in most cases, to determine the inorganic constituents. The predominating organic fraction was either not considered at all, or was analyzed for total carbon, hydrogen, oxygen, and nitrogen. Frequently, the calorific value of peat was also determined. In a number of instances, however, an analysis of the ether- and alcohol-soluble constituents was made, and, in fewer cases, an attempt was also made to determine the presence of definite organic complexes, such as pentosans, celluloses, proteins and their derivatives. Very few cases are recorded, of an approach to a more than general estimation of the nature of the organic complexes in peat.

The presence in peat of a number of the so-called "humic acids" has received detailed and frequent consideration. A study of these, which dates back to the beginnings of our systematic knowledge of peat formations, has contributed but little to our understanding of the nature of the organic matter. It is not even known whether these "humic acids" exist in peat in a free state or have been formed as a result of the action of the chemical reagents used in their separation from the peat. The various formulas suggested for the different humic, ulmic, crenic, and other acids are not based upon sufficient experimental evidence. These hypothetical complexes, even if justified by some hypothetical considerations, are based on very few facts. One frequently

wonders, after an analysis of much of the evidence on the so-called "ulmins" and "humins," "ulmic acids" and "humic acids," etc., just how much progress has been made, during the last century of investigation, in our understanding of the chemistry of the organic complexes in peat materials.

A more detailed knowledge of the nature of organic matter in peat is desired for at least two important reasons:

1. Such knowledge, even if largely of theoretical interest, would help us gain an insight into the origin of this mass of natural organic matter. By comparing the chemical composition of peat with that of the plants which gave origin to it, we can readily determine the nature of the processes which take place in peat formation. The importance of such knowledge can hardly be overemphasized. This becomes especially evident when one considers the fact that many peat experts and outstanding coal chemists still consider the processes involved in peat formation entirely chemical in nature, and do not attach any importance to the rôle of microorganisms in these processes.

2. A more exact knowledge of the chemical composition of peat would materially advance its practical utilization, both for agricultural and industrial purposes.

Our information concerning the chemical nature of peat depends largely upon the methods of analysis which are frequently found to be wanting. Dachnowski (2), having attempted to apply the methods of the food chemist to the study of the composition of peat and differentiate it into digestible and indigestible fractions, failed to establish important differences between different peat materials. He came, therefore, to the conclusion that these methods of analysis "do not give sufficiently forceful illustration of the available organic compounds in plant remains now stored as layers of peat."

Still less definite information is available concerning the rôle of microorganisms in the formation and transformation of peat although various studies have been made in regard to the presence in peat, especially in peat soils, of organisms commonly found and considered of importance in ordinary field and garden soils. The various microbiological studies dealing with the presence in peat soils of organisms capable of decomposing proteins or with the absence of organisms capable of forming nitrates, contribute little to our understanding of the processes of peat formation under natural conditions, or of transformations taking place in peat when the natural bogs have been drained and cultivated and the bog changed into a soil.

Our ideas concerning the origin of peat have recently been considerably stimulated and definite information gained from the various theories and hypotheses proposed by such eminent chemists as Fr. Fischer (5), Bergius (1), Marcusson (17), and others to explain the rôle of celluloses and lignins in the formation of peat and coal.

HISTORICAL

A detailed review of the extensive literature dealing with the chemical composition of peat need not be attempted here. Attention will be called only to certain recent contributions which have served to advance our understanding of this subject and bring some system into the complicated and uncorrelated

mass of facts that have previously accumulated. These comprise both the inorganic and the organic chemical complexes of peat, the nature of which depends entirely upon the kind of the plants and plant remains from which the peat has originated, the conditions under which peat formation has taken place, and the processes of decomposition thereby involved.

It has been pointed out above that peat formation takes place under anaerobic conditions, because the plant residues decompose in a bog covered or saturated with water. The roots of the plants grow either directly in the water or in the mass of dead plant residues which is saturated with water. Under these conditions, an accumulation of organic matter takes place as a result of its incomplete decomposition. The process of peat formation (*Vertorfung*) is thus distinguished from the decomposition of plant and animal residues in normal aerated soils (*Verwesung* or *decay*). In the latter process, the plant residues are, with relative rapidity, sooner or later completely decomposed and are changed into simple inorganic and organic compounds, leaving only a small part of dark-colored material or so-called "humus" which is more resistant to decomposition. This residual "humus," however, is hardly sufficient even to replenish the losses of the soil organic matter or soil "humus," since these residues which have been left from previous crops, are still undergoing decomposition, especially under systems of intensive cultivation. If the conditions under which organic matter is formed or laid down favor even partial anaerobiosis, as in the case of virgin soils and pastures, organic matter may gradually accumulate. If a system of intensive cultivation is used without the introduction of stable manure or green manures, the residues left from the growing plant will not be sufficient to replenish the supply of soil organic matter which is constantly being decomposed by microorganisms under favorable conditions of aeration, moisture and reaction.

In peat formation, most of the aerobic organisms are largely excluded, except upon the very surface, and the activities of the anaerobic bacteria are hardly sufficient to break down more than a part of the plant residues which are added annually by the growing plants in the form of roots, rhizomes, pollen, spores, leaves, needles, and twigs. The most important chemical problem in regard to the nature of peat is to determine whether this mass of accumulated organic matter results from the incomplete decomposition of all plant constituents, or whether some of the plant constituents are readily decomposed and others, which are more resistant to decomposition, accumulate under anaerobic conditions and give rise to peat.

The presence in peat of the so-called "humic acids" has been frequently taken as a measure of peat formation. The material was extracted with different alkalies for different lengths of time. An aliquot portion of the solution was either evaporated to dryness (when ammonia was used as the solvent), or the "humic acid" was precipitated from the solution with hydrochloric acid, or the color of the solution was compared with that of an alkaline extract of some standard "humus" preparation. The residue left

after evaporation, the precipitate, or the depth of color of the solution, was taken to indicate the amount of "humic material" in the peat; this served as an index of "peat formation." However, it was found that different alkalies, in different concentrations, at different temperatures, will extract different amounts of "humic matter" from the same peat. Schneider and Schellenberg (28), for example, reported that, at room temperature, a 5 per cent solution of NaOH will dissolve 10.7 to 34.8 per cent of peat, whereas a 5 per cent solution of NH₄OH will dissolve only 2.4 to 21.5 per cent of peat. The higher the temperature of extraction, the greater is the amount of material extracted; a considerable amount of organic matter (especially the important element nitrogen in the form of ammonia) is thereby lost on volatilization. The longer the period of extraction and the greater the pressure, the larger is the amount extracted.

For these reasons and because the nature of the substances extracted by alkalies and precipitated by acids present rather difficult and highly confusing problems, the use of alkalies for determining the nature of peat and for obtaining quantitatively the amount of so-called "humic" or "humified" matter in peat may be abandoned.

The methods suggested by Robinson (26)—treatment of organic matter with a 6 per cent hydrogen peroxide solution—, by König (14)—treatment of material with 3 per cent hydrogen peroxide and ammonia—or by Karrer and Bodding-Wiger (11)—treatment of peat with acetyl bromide—, even if enabling us to determine quantitatively certain organic complexes which have been formed or have accumulated as a result of incomplete decomposition of natural organic matter, throw little or no light on the chemistry of these organic complexes in soil and in peat.

A knowledge of the chemistry of peat, or of the chemical composition of the various organic complexes that make up the peat material, necessitates an understanding of: first, the chemistry of the plant residues which make up the peat bogs, and, secondly, the microbiological and chemical processes which are involved in the transformation of the plant materials, whereby these give rise finally to peat.

In this connection, three theories concerning the processes involved in the formation of peat must be considered. These may apply both to the formation of "humus" in ordinary soil and to the formation of coal. It is assumed that the types of processes which give rise to the organic complexes in field soils, in peat, and in coal are similar in principle, although they may vary considerably in detail, because of the differences in the plant and animal residues, in the environmental conditions under which decomposition is taking place and in the microorganisms active in some or all of the stages of decomposition.

Theory 1. The older theory of the geologists and botanists, and recently of some chemists (23, 16), that the celluloses—the largest single group of organic complexes in natural plant materials—give rise, by processes of slow chemical oxidation, to dark colored substances, which finally result in the formation of peat, and later of coal.

Theory 2. The more recent theory of Fischer and Schrader (6), who claim that when fresh natural organic matter undergoes decomposition, the celluloses and hemicelluloses are rapidly broken down by microorganisms, while the lignins, resins, and waxes resist decomposition and, therefore, accumulate. From the point of view of this theory, peat formation may be looked upon as a gradual accumulation of lignins and, to a less extent, of certain other natural plant constituents.

Both of these theories are based entirely upon chemical considerations of processes of transformation of certain large groups of plant constituents. The geologists and botanists were satisfied in their ideas that celluloses, the woody, cutinized and corky substances of plants, give rise to peat and later to coal, without attempting to prove experimentally whether this is actually taking place in nature when plant residues are undergoing decomposition. The chemist has gone only one step further and has attempted to determine, by the use of chemical reagents, whether celluloses and lignins can be changed into "humic acids" and coal. However, insufficient consideration has been given to the fact that plants contain various other chemical constituents, in addition to celluloses and lignins, especially the nitrogenous complexes, and that the resulting soil "humus," peat, and even coal always contain a definite proportion of nitrogen. The transformation of the organic matter takes place in nature, at least until the peat stage, through the agencies of microorganisms and not by chemical oxidations at 340°C.

The supporters of the first theory based their conclusions upon the fact that although peat may contain only 7 to 15 per cent cellulose, it contains 50 per cent of other polysaccharides, which are considered as oxycelluloses and which were believed to be derived from true celluloses through the action of air, light, and moisture. The oxycelluloses are believed to give rise to "humal acids" and these to "humic acids" which are soluble in dilute alkalies (16, 17). It was also shown chemically that "humic acids" can be derived from cellulose and need not be considered only as lignin derivatives.

Fischer (6, 7), brought the following evidence in support of his theory:

1. The experiments of Rose and Lisse (27) have shown that with an increase in the decomposition of wood there is a decrease in the cellulose content and an increase in the methoxyl (a group characteristic of lignin) content and of the alkali-soluble material.
2. Peat shows, with an increase in depth, an increase in the methoxyl content, an increase in the alkali-soluble material, and an increase in the material which is insoluble in concentrated hydrochloric acid.
3. Although cellulose and wood added to a liquid culture medium allow abundant development of fungi and bacteria, lignin does not.
4. There is a certain similarity in the chemical composition of peat and coal and of lignin (phenol structure) as contrasted with that of cellulose (furan structure).

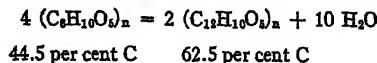
According to Marcusson (16), however, the increased methoxyl content, found by Rose and Lisse in decomposing wood and used by Fischer as one basis for his theory of origin of coal from lignin, is due to the methoxyl of the pectin of the wood, whereas the increase in the alkali-soluble substances is due to the increase in the oxycelluloses. By repeating the results of Rose and Lisse,

using Cross and Bevan's method for cellulose determination and Wilstätter's method for lignin determination, the cellulose content of wood was found to diminish from 58 per cent in the healthy wood to 6 per cent in the decomposed wood; the lignin content increased from 25 to 44 and 37 per cent. However, when the wood was first treated with 1 per cent solution of NaOH for 1 hour on a boiling water bath, the lignin content in the residue was found to be practically the same in the decomposed as in the healthy wood material. The material soluble in dilute alkali is presumably due to the "humic acid" (of which there was only 0.7 per cent in healthy wood and 12.1 per cent in decomposed wood), which originated from the cellulose, by processes of hydrolysis and oxidation, through the oxycellulose stage.

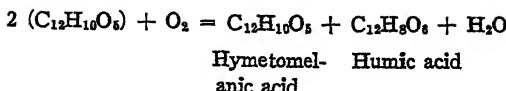
The fact that the nature of the lignin in sphagnum plants is still questioned, when compared with the lignin of higher plants, serves further to complicate these theories. The results of peat analysis, which are based upon the lignin content of sphagnum are open to criticism, since, when calculated from the methoxyl content, the lignin content of sphagnum is found to be only 3 per cent; when calculated on the basis of the material which is insoluble in concentrated hydrochloric acid, the lignin content of sphagnum may go up to 9 to 13 per cent; and finally, when extracted with alkalies or sulfurous acid, as much as 75.8 per cent may be recorded as lignin, most of this material consisting of course, largely of hemicelluloses. Oden and Lindberg (21), for example, found that with increasing decomposition of sphagnum ("humification"), there is a decrease in the sulfite-soluble material and in the cellulose and an increase in the ammonia-soluble material.

Thaysen and associates (30) found that the "humin" complexes obtained from peat can be divided into two groups: one giving a chlorine derivative which is identical or similar to that of lignin, the other giving a chlorine derivative which is similar to that of artificial humus obtained by the action of inorganic acids upon cellulose. It is believed that the second group is formed from the cellulose which is not decomposed by microorganisms.

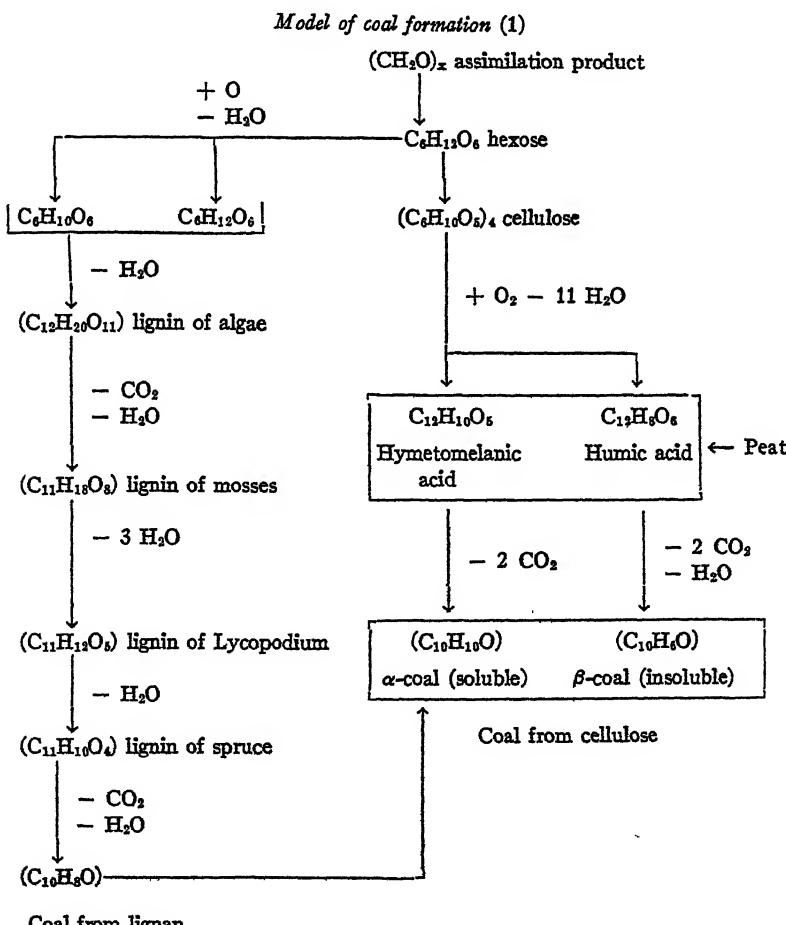
The ideas of Bergius (1) tend to combine the two theories outlined and give place to both celluloses and lignins as the mother substances of peat and coal, which are formed under proper conditions of temperature and pressure and after a definite length of time. Bergius found that, at 250°C., cellulose gives a product which is considerably richer in carbon and which becomes partly soluble in alkali, when allowed to take up oxygen:



The product thus obtained can be separated into two groups, on the basis of its solubility in alcohol, thus giving an alcohol-soluble hymetomelanic acid and an alcohol-insoluble humic acid (according to Oden's nomenclature), both of which are found in soil and in peat.



Coal can be obtained from both lignin and cellulose when these are heated to 340°. This coal consists of two forms: α -coal, soluble in alcohol and in NaOH solution, and β coal, which is insoluble in these solvents. The only difference between the coals is that lignin gives 50 per cent α -coal and 50 per cent β -coal whereas cellulose yields a coal which consists of 70 per cent α and 30 per cent β . Bergius suggested the following hypothesis which tends to explain both the origin of lignin in different natural products and the processes of formation of "humus," "peat," and "coal":



Theory 3. A theory (31-33) which takes into consideration largely the activities of the microorganisms which decompose the natural plant and animal residues and give rise to peat or to soil organic matter.

An attempt was made to explain a number of confusing points in the first two theories. According to this theory, some constituents of natural organic materials (sugars, amino acids, starches, certain hemicelluloses, proteins) are rapidly decomposed by microorganisms under favorable conditions; some of the other plant constituents (celluloses, oils, certain fats, and certain hemicelluloses) are readily but somewhat more slowly decomposed; while certain plant constituents (lignins, waxes, cutins, certain hemicelluloses) are resistant to decomposition, especially under anaerobic conditions.

Under aerobic conditions (as in the case of field and garden soils, forests, pastures not saturated with water), the first two groups of plant constituents are rapidly decomposed. The decomposition of the substances placed in the first group is independent of the amount of available nitrogen in the soil. The decomposition of the constituents of the second group is controlled by the liberation of available nitrogen. The substances placed in the third group of plant constituents are more resistant, but they still undergo a slow decomposition, which is carried out by actinomycetes and by certain bacteria in field and garden soils and by certain fungi belonging to the basidiomycetes in forest soils. This is why organic matter does not accumulate greatly in well aerated soils, unless the physical conditions become unfavorable to the activities of microorganisms, as in the case of certain forest ("raw humus") soils.

Under anaerobic conditions, as in the case of peat soils, the constituents of the first group of substances are rapidly decomposed; the representatives of the second group are decomposed more slowly; the rapidity of decomposition being here again controlled by the amount of available nitrogen and minerals. However, in view of the fact that the conditions are not favorable for the activities of aerobic bacteria and fungi, the decomposition of celluloses has to be carried out largely by anaerobic bacteria. The reaction of highmoor peat bogs [pH 3.2-4.2 (15)] may then become unfavorable even for the activities of these organisms. The third group of substances does not decompose at all under anaerobic conditions, because these conditions are extremely unfavorable for the activities of the specific actinomycetes, basidiomycetes and bacteria, which bring about the decomposition of those substances under aerobic conditions. The growth of microorganisms, which use the substances of the first two groups as sources of energy, results in the synthesis of considerable quantities of cell substance, some of which is resistant to further decomposition. It is this cell substance which accounts for the nitrogen content of the soil organic matter under aerobic and probably also under anaerobic conditions.

Several other theories have been suggested that tend to explain the origin of soil "humus," through synthetic chemical processes, either as a result of oxidation of benzene ring compounds, or interaction of carbohydrates with amino acids, or polymerization of furfural. A detailed discussion of these theories has been presented elsewhere (31).

Before going into a discussion of the chemistry of peat, it is important to call attention to the fact that the various types of peat may differ considerably

in chemical composition, just as they differ in the nature of the plants which gave origin to the peat, in the chemical composition of the medium in which the plants were growing and in the composition of the plants themselves. Several distinct types of peat are at present commonly recognized:

1. *Lowmoor peat* (Niederungs—or Flach-moor, marsh) is formed by specific plant associations in which sedges and reeds (species of *Carex*, *Phragmites*, *Cladium*, etc.) play the most important part; certain trees and shrubs may also play a part. This type of peat is usually formed in places where the waters, containing calcium and rich in nutrients, are of telluric origin and drain slowly into lower regions or inclined planes.

2. *Highmoor peat* (Hochmoor, moor, or moor peat) is formed by plant associations in which the predominant vegetation consists of species of *Sphagnum*, *Eriophorum*, *Calluna*, and various other shrubs and trees. This type of peat is formed in waters containing little calcium and poor in mineral nutrients, originating from atmospheric precipitation or from mineral poor soils.

3. *Forest peat*, formed by various trees, with an admixture of shrubs (*Calluna*, *Oxycoccus*, etc.), reeds, and sphagnum moss. This type of peat commonly occurs at the end of sphagnum bogs and may even cover the whole bog; it is fed partly by ground waters and partly by precipitation.

In addition to these three main types of peat, various combinations of these and certain other types are recognized. The most important of these other types of peat is the sedimentary materials or mud peat (Gyttja, Lebertorf, Dy) formed largely by algae and other aquatic plants and animals, with an admixture of spores, pollen, and particles of clay and sand. It is usually found in the lowest layers of peat deposits and is referred to frequently as *lake peat*, *mud*, or *gyttja* (22).

Without going into a detailed discussion of the plant associations in the different peat profiles, it may be stated here that the stratification of the peat deposits is directly related to the changes in the wet and dry periods which accompany changes in climatic conditions.

The lowmoor peats are usually less acid and contain more mineral matter (especially calcium) and nitrogen than the highmoor peats. In the lowmoor peats there is a gradual increase in the nitrogen content from the plant to the peat. In the highmoor peats, however, there is an actual decrease in the nitrogen content when the plant is changed into peat. This difference may be due to either of two causes: 1. The celluloses decompose more rapidly in the lowmoor- peat-forming plants, than in the *Sphagnum*, *Calluna*, and *Eriophorum* plants, some of which are rich in rather resistant hemicelluloses; and micro-organisms rapidly assimilate the nitrogen liberated from the proteins. 2. The nitrogen complexes are more rapidly decomposed in the sphagnum plants and the ammonia which is liberated as a result is immediately assimilated again by the growing parts of the plants, which must be very economical in their nutrition in a medium as poor as that represented by a highmoor bog. There is also a diminution in the phosphoric acid and potash content when plants are decomposed to give rise to peats.

The most important problems in connection with the study of the chemistry

of peat, its origin or the formation and accumulation of organic matter under the particular conditions, and, finally, its decomposition, are largely concerned with the organic complexes which make up 50 to 99 per cent of the dry matter of the peat. This organic matter has been studied only to a very limited extent. It includes oils, fats, and waxes; celluloses; hemicelluloses; pectins and other carbohydrates and related compounds; lignins; organic acids; nitrogenous complexes, not all of which are protein in nature; and various other substances. The ether- and alcohol-soluble organic constituents of peat have been studied most extensively and important differences have been established between different peats (18, 19). In the case of pollen peat, for example, the ether- and alcohol-soluble fractions were found to make up almost one-third of the total organic matter. With an increase in the age of peat, there was also found to be an increase in these fractions, but different peat formations vary in this respect.

The cellulose and hemicellulose content of peat was studied only to a limited extent. Von Feilitzen and Tollens (4) found that with an increase in the degree of decomposition of peat, there is a decrease in the cellulose and pentosan content. Schneider and Schellenberg (28) could not demonstrate, however, any cellulose in peat. The difference may be due to the fact that different peats were used in these two investigations; it will be shown later that some peats may contain considerable quantities of true celluloses, whereas other peats may be entirely free from celluloses, although showing a high hemicellulose content.

The chemical constituents of peat can be divided, on the basis of the results of Zailer and Wilk (37), into 4 groups:

1. Constituents of the original plant materials, comprising ether-soluble, alcohol-soluble, and water-soluble organic and inorganic complexes as well as various cell substances (lignin, cellulose, etc.).
2. Transformation products of the plant materials, comprising the so-called "humic acids," "indifferent humus," "humates," "ulmatae," and intermediary products of a colloidal nature.
3. Ash constituents.
4. Water.

In referring to these results, Hoering (9) remarks that whereas groups 1 and 2 may be of scientific interest, groups 3 and 4 are largely technically important.

Keppeler (12) suggested that the chemical constituents of peat be divided into two fractions, on the basis of their reactivity to 72 per cent sulfuric acid. This treatment changes all the celluloses and hemicelluloses to glucose. The amount of reducing sugars thus formed was used as a measure of the polysaccharide content of the peat. The pentosans were determined separately by the phloroglucide method. The difference between the total reducing sugar and the pentosans gives the hexosan content of the peat.

As a result of these studies, Keppeler suggested the following formula as a measure of the degree of decomposition of peat:

$$\left(100 - \frac{\text{total reducing sugar} \times 100}{\text{68}} \right)$$

68 being the amount of reducing sugar commonly found by treating sphagnum plants with 72 per cent acid solution. With an increase in the depth of peat, a decrease in the total reduction and, therefore, an increase in the degree of decomposition were found. The residue left after treatment with the concentrated acid (ash-free lignin) was taken as an index of peat formation (Vertorfung). This index was found to be comparable with the degree of decomposition.

This method does not tell, however, whether there is a difference between the hemicellulose (exclusive of the pentosans) content of the peat and the presence of true celluloses. The important nitrogenous complexes are not considered at all. The degree of decomposition is calculated by the use of a very arbitrary figure, found in the analysis of sphagnum, which can be applied at best only to highmoor peat. Gorbenko (9) found this method to be inaccurate and too complicated for practical purposes.

A knowledge of the chemical nature of peat necessitates an understanding of the chemical composition of the plants which gave origin to the peat and a knowledge of the processes of decomposition as well as of active agents which cause plant residues to be changed into peat. A definite system of analysis of the organic matter therefore must be adopted, which would give, if not absolutely complete results concerning the chemical composition of peat, at least a proximate sum of its constituents. It is the purpose of these investigations to utilize such a method of analysis and also to throw light upon the problem of peat composition and formation. An attempt will be made later to show how these results will help us to understand the mechanism of decomposition of peat, when conditions are made favorable by drainage, cultivation, and fertilization.

METHODS OF ANALYSIS

Because peat is largely organic in nature and has originated largely from plant materials, the methods of analysis which were found useful in the study of the composition of natural plant materials (4, 29, 34) and especially in the study of the decomposition of these materials by microorganisms (34) can also be applied, with certain modifications, to its analysis. By the use of these methods, not only can definite information be obtained in regard to the presence in peat of certain organic complexes of a definite chemical nature, but one can also compare the relative transformation of these complexes, from the original plant materials to the peat.

The methods used in these studies may be briefly outlined as follows:

Whenever possible, the samples of peat were taken fresh from the bog, in certain definite strata or horizons, and careful notes were made in regard to the surface vegetation, depth of profile, and botanical composition of samples. As soon as the samples were brought to the laboratory (usually within 24 hours) the moisture content of the natural product was determined. For chemical investigations a part of the sample was allowed to air dry at room temperature. This air-dry material was used for all the analyses and the results are calculated on an oven-dry basis. The reaction of the material was determined by means of the quinhydrone electrode. Fresh samples of lowmoor or forest peats and of a mixed peat were obtained within a short distance from the laboratory. The lowmoor peat samples were obtained from a peat bog near Newton, N. J., through the courtesy of the Hyper-Humus Co. Samples of the highmoor peat (in an air-dry state) were placed at the disposal of the writers by Dr. A. P. Dachnowski-Stokes, of the Bureau of Chemistry and Soils, Washington, D. C., from a profile of Oldenburg (Germany) peat, taken in 1924.¹

Separate portions of the air-dry material are used for the determinations of moisture content, reaction, and total nitrogen and ash content. The complete analysis is usually carried out on two 5-gm. portions of peat material, and the results are calculated on the basis of dry weight. The process is carried out as follows:

The peat is first extracted with sulfuric ether in Soxhlets for 16 to 24 hours; the ether-soluble portion of the peat is then determined by evaporating the ether, then drying the residue in weighing bottles until constant weight is attained. The residue left after the ether treatment, is extracted for 24 hours with cold distilled water, to give the cold-water-soluble fraction; an aliquot portion of the aqueous solution is evaporated to dryness in weighed silica dishes on a water bath, then dried, weighed, ignited, and weighed again, thus giving the water-soluble organic matter and ash; another portion of the extract is used for the determination of total nitrogen; nitrates and reducing sugars may be determined in other portions of the extract. The residue from the cold-water extraction is now treated with hot water for 1 hour on a water bath. This extract is usually analyzed for soluble organic matter and nitrogen. After the ether and water extractions, the material is treated two or three times with 100-cc. portions of boiling 95 per cent alcohol. This extraction is continued for about 1 to 2 hours. The filtered solutions are combined and evaporated, in weighed dishes, to constant weight.

The residue left after treatment with alcohol is extracted for 5 hours with 100 to 150 cc. of a 2 per cent solution of hydrochloric acid, at 100°C., under a reflux condenser. Autoclaving for 1 hour at 1 atmosphere pressure is just as effective, although the celluloses may be somewhat attacked by this treatment than by the previous one. The hot extract is filtered through filter paper which has been previously dried and weighed; the residue is washed into the filter and treated with distilled water until free from acid. The combined filtrate and washings are analyzed for total nitrogen and for total reducing sugar (an aliquot portion of the solution having been previously neutralized with 40 per cent NaOH solution). This sugar is derived from the hemicelluloses in the peat, which are hydrolyzed by the dilute acid, while the true celluloses are affected only to a very limited extent. The total reducing sugar found in the acid extract may be reported either as hemicellulose sugar or may be multiplied by 0.9 to give the hemicellulose content of the peat. One must keep in

¹ The authors take this opportunity of expressing their sincere appreciation to Dr. Dachnowski-Stokes for this courtesy as well as to Dr. E. Melin for assisting in the identification of the plant ingredients.

mind the fact that this figure, although frequently considerably larger than the figure for pentosan determined by the phloroglucide method, represents only a minimum and is usually considerably lower than the total organic matter soluble in dilute hydrochloric acid. This is because various complexes, like the pectins, gums, methyl pentosans, and certain glucosides, give sugar only as a part of the hydrolytic products, whereas certain plant residues, like mosses, contain polysaccharides which are hydrolyzed only after prolonged boiling with dilute acids.

The residue left on the paper, after the treatment with dilute acid, is dried for 24 hours at 70°C. and weighed. The weight of the residue is obtained by subtracting the weight of the paper from the total. In the case of sphagnum or young sphagnum peat, before being dried the material must be washed with alcohol and then with ether, to give a properly dried product. Two 1-gm. portions of the dried residue are taken from each of the duplicate preparations and treated with 10-cc. portions of an 80 per cent solution of sulfuric acid; the acid is allowed to act in the cold for 2 hours (13). If the material does not mix well with the acid, it must be broken with a glass stirring rod. At the end of 2 hours, 150-cc. portions of distilled water are added to each flask and the contents are boiled for 5 hours under a reflux condenser or autoclaved for 1 hour at 1 atmosphere pressure. The extracts are now filtered

TABLE I
Proximate chemical composition of a lowmoor and highmoor peat
(On per cent basis of dry material)

CHEMICAL CONSTITUENTS	LOWMOOR PEAT	HIGHMOOR PEAT
Ether-soluble fraction.....	0.43	4.34
Soluble in cold and hot water.....	1.71	1.61
Alcohol-soluble fraction.....	1.94	3.40
Hemicelluloses.....	11.03	15.76
(Pentosan).....	(2.52)	(3.60)
Celluloses.....	0	12.35
Lignin.....	44.81	44.19
Crude protein.....	20.97	4.94
Ash.....	13.02	1.82
Total accounted for.....	93.91	88.41

either through weighed Gooch crucibles or through small dried and weighed quantitative filter papers. The residue is washed thoroughly with distilled water, dried at 70°C., and weighed. One of the residues from the duplicate original preparations is now ignited to determine the ash and the other residue is used for a determination of total nitrogen. The weight of the residue after the sulfuric acid treatment, minus the sum of the weight of the ash and of the total nitrogen which has been multiplied by 6.25, gives the lignin in 1 gm. of the material left after the treatment with dilute hydrochloric acid. The weight of this lignin when multiplied by the weight of the material not dissolved in the 2 per cent HCl gives the lignin content of the original 5 gm. of peat material. The solution and filtrate from the H_2SO_4 treatment are analyzed for sugar, an aliquot portion having been neutralized previously with 40 per cent solution of NaOH. The reducing sugar multiplied by 0.9 gives the cellulose content of 1 gm. of material left after the HCl treatment. The cellulose figure multiplied by the weight of the material not dissolved in 2 per cent HCl solution will give the cellulose content in the original 5 gm. of peat material.

The method of analysis outlined here can be used very conveniently for the study of the proximate chemical composition of natural plant materials, microbial cell substance, organic matter in the process of decomposition, and of soil organic matter, especially in the case of soils which are low in inorganic matter, such as forest soils and peat soils. The methods may be variously modified, by leaving out the cold-water-soluble fraction in the case of peats, which, being formed in a medium saturated with water, contain little of cold-water-soluble constituents. This method of analysis enables us to bring out the differences in composition not only between different types of peat but also between the different profiles of the same peat, which have been subjected to different weathering conditions, and between the organic matter of natural peats and of peat soils. The results thus obtained help us to visualize at a glance what has taken place in the processes of formation of peat for natural plant materials and further what is taking place when a peat bog is drained and changed into a soil.

By the use of this method of analysis, the natural organic matter and peat materials can be divided into the following groups or fractions:

1. *The ether-soluble fraction.* Ether extracts from plant substances and from other organic materials the ethereal and fatty oils, a part of the wax-like and resin-like substances, certain nitrogenous fats, etc.

2. *The water-soluble fraction.* Cold water extracts from the plant residues and from the other natural organic materials the sugars (glucose, mannose, sucrose, pentoses), amino acids, certain soluble proteins, organic acids (malic, tartaric, acetic, citric, arabinic, etc.), alcohols (mannitol, etc.). Although this fraction is quite considerable in the case of undecomposed plant materials, especially in young growing tissues, peat contains very little of this fraction. Hot water extracts some of the starches, tannins, and pectins as well as certain amino acids, organic acids, etc.; this fraction as well is not very abundant in peat, so that both can be combined, or even left out.

3. *Alcohol-soluble fraction.* 95 per cent alcohol extracts from plant materials and from peats the phlobaphenes, waxes, resins, bitter substances, alkaloids, chlorophyll and other pigments, tannins, terpenes, choline, higher alcohols (inositol), etc. In some peats the ether- and alcohol-soluble fractions may contain as much as one-third of all the organic matter. According to Zailer and Wilk (37), there is in sphagnum peat an increase in the ether-soluble (from 1.16 to 5.58 per cent) and in the alcohol-soluble (from 2.98 to 11.16 per cent) fractions with an increase in the degree of decomposition. This does not hold true, however, in the case of other peats, Minssen (19) having actually found a decrease in the two fractions with an increase in depth of a Carex peat.

4. *The hemicellulose fraction.* This group comprises those carbohydrates which are not soluble in water but which are soluble in boiling dilute acids. The hemicelluloses include both pentosans and hexosans (arabans, xylans, galactans, mannans, manno-galactans, and various glucans). In the higher plants, the pentosans predominate, so that a direct determination of pentosan by distillation with 12 per cent hydrochloric acid and precipitation with phloroglucin may be sufficient. However, in the case of sphagnum and microbial cell substance, the pentosans occupy only a secondary part and frequently only a minor part of the hemicellulose group. This is especially true of peat, where there is frequently found 3 to 4 times more total hemicellulose than pentosan. In view of this, the determination of the total hemicellulose content is essential. A pentosan determination may be made on a separate portion of material. It will be found that even if pentosan-rich plants give rise to peat,

as in the case of lowmoor and forest peats, the pentosans decompose more or less readily, while the hexosan-hemicelluloses accumulate, either because those present in plants are more resistant to decomposition than the pentosans or because some of them are synthesized by microorganisms and are more resistant to decomposition.

5. *The cellulose fraction.* This group comprises the true celluloses, or those carbohydrates which are not soluble in hot dilute inorganic acids but are soluble in concentrated acids, such as 72 to 80 per cent sulfuric or 42 per cent hydrochloric, giving glucose as the only product of hydrolysis. Among the various plant constituents, especially the residues which are turned back to the soil, the true celluloses occupy the first place in relative abundance. However, in the cell substance of the mosses and lichens, in the fungus and algal cells, the hemicelluloses may be more abundant than the true celluloses. In the case of fungi, the fungin, fungus cellulose, or chitin takes the place of the true cellulose. The difference between the fungus cellulose and true cellulose of higher plants consists in the presence in the former of a nitrogen and an alcohol group, in addition to the glucose.

6. *The lignin fraction.* Lignins are chemically less defined than celluloses and hemicelluloses, fats, waxes, and most other major plant constituents. They can be determined either by extraction with alkalies under pressure and precipitation with inorganic acids, or by treating the plant material with concentrated hydrochloric (42 per cent) or sulfuric (72-80 per cent) acid; this treatment leaves the lignins undissolved. In view of the fact that methoxyl forms a characteristic group of the lignin molecule, the methoxyl content is frequently taken as an index of the amount of lignin present. But since not only lignin from various plants, but also lignin from different parts of the same plant contains varying amounts of methoxyl (24), this method of quantitative determination of lignin is open to question (16). The amount of lignin obtained by treatment with an alkali solution followed by precipitation with acid, depends largely upon the nature and concentration of alkali used, the temperature and pressure at which the extraction is carried out, as well as the nature of the acid used for precipitation and the temperature at which the precipitation is carried out. For chemical studies of the nature and composition of lignin, this method is quite convenient, especially when followed by further purification. However, for rapid determination of lignin in plant material, it can hardly be recommended. On the average, the yield of alkali lignin represents usually only about one-half of the acid lignin. This relation can be readily explained by accepting the theory of Bergius (1) discussed above. Although the various modifications for the quantitative determination of lignin by the acid treatment are also each open to one criticism or another, this method represents at the present time the most convenient that we possess.

7. *Nitrogen groups in peat.* The nitrogen content of peat is recorded in the following investigations as crude protein (this is calculated by multiplying the difference between the total nitrogen and the water-soluble nitrogen by 6.25). This does not mean, however, that all the nitrogen is present in peat in the form of proteins; probably a large part of the nitrogen is of a non-protein nature. As a matter of convenience, however, all the insoluble nitrogen may be recorded as protein. From the results presented below, the following three groups of nitrogen complexes may be recognized: 1. The water-soluble compounds including various amino acids and soluble proteins, ammonium salts, and nitrates. 2. Nitrogen compounds (largely proteins) hydrolyzable and giving water-soluble compounds on boiling for several hours with dilute acid. 3. "Humin" nitrogen, or that part of the nitrogen which is not acted upon by dilute acid at 100°C. or by concentrated acids in the cold. By adding to these 3 groups the nitrogen made hydrolyzable by boiling with more concentrated acid (H_2SO_4 soluble fraction), all the nitrogen in the peat could be accounted for.

8. *The ash or inorganic fraction of peat.* Because the mineral composition of peat and of peat-forming plants has been the subject of a number of investigations, no detailed analyses were carried out in these studies. This fraction is reported only as total ash.

A proximate analysis of two different types of peat, one a lowmoor taken at the surface of a Carex bog at Newton, N. J., and the other a typical highmoor or sphagnum peat from Oldenburg, Germany is given in table 1. The lowmoor peat had a pH of 6.0 and was rich in nitrogen and minerals, while the highmoor peat had a pH of 4.1 and was characteristically low in both nitrogen and minerals.

The results show that there is a marked difference in the chemical composition of the two types of peat. Both are poor in water-soluble constituents and rich in lignins or lignin-like complexes. The lowmoor peat is entirely free from true celluloses and has 11.03 per cent hemicellulose, of which only a small fraction is pentosan; the highmoor peat is still rich in celluloses and contains more hemicellulose than the lowmoor peat. The highmoor peat is poor in protein and ash, while the lowmoor peat is rich in both. The highmoor peat contains considerably larger quantities of ether-soluble and more alcohol-soluble materials. These differences are sufficient to throw light not only upon the chemical composition of the peat materials, but also to bring out the

TABLE 2
Nitrogen distribution in 100 gm. of lowmoor and highmoor peat

PEAT MATERIAL	LOWMOOR	HIGHMOOR
Total nitrogen found.....gm.	3.702	0.815
Soluble in cold and hot water.....gm.	0.089	0.026
Soluble in hot dilute acid.....gm.	1.908	0.343
"Humin" nitrogen.....gm.	1.258	0.414
Total accounted for.....gm.	3.255	0.783

changes in the chemical nature of the organic materials in the process of peat formation. In the decomposition of the carex, phragmites, and other lowmoor peat-forming plants, the celluloses and practically all the pentosans have disappeared, while a large part of the hemicelluloses, largely hexosans in nature, are left. There was an increase in the protein content due to the synthesizing activities of microorganisms. In the highmoor peat, a large part of both celluloses and hemicelluloses are left and much less synthesis has, therefore, taken place.

The nitrogen distribution in the two peat materials is given in table 2. The water-soluble nitrogen is very low in both types of peat, comprising not more than 2.5 to 3.0 per cent of the total nitrogen. The nitrogen fraction which is made soluble by treatment with boiling dilute acids varies considerably, depending on the concentration of the acid, period of extraction, temperature and pressure at which the extraction is carried out, etc. This fraction may thus account for 30 to 65 per cent of the total nitrogen in the peat. This fact has been brought out by Jodidi (10), Robinson (25), and others. The so-

called "humin" fraction (this does not correspond to the "humin" fraction of proteins as commonly understood), or that part of the nitrogen which is not acted upon at all by hot dilute acids or by cold concentrated acids is relatively abundant in peat. It comprises one-third of the total nitrogen in the lowmoor and one-half of the nitrogen in the highmoor peat. One must remember that this nitrogen fraction has resisted treatment for 5 hours with boiling dilute hydrochloric acid, for 2 hours with 80 per cent sulfuric in the cold, and then for 1 hour heating at 120°C. with 5 per cent sulfuric acid (the concentrated acid diluted 16 times).

The most important conclusion to be drawn from these analyses is that by the method outlined above, one can account for 88.4 to nearly 94 per cent of the constituents of the peat in terms of definite chemical groups. It will, of course, remain for later studies to determine the nature of the hemicelluloses,

TABLE 3

Influence of acid concentration and repeated extraction upon the hemicellulose and nitrogen brought into solution

10 gm. of dry lowmoor peat extracted with 100 cc. acid

CONCENTRATION OF HCl <i>per cent</i>	NUMBER OF EXTRACTIONS	HEMICELLULOSE	TOTAL NITROGEN IN SOLUTION
		<i>mgm. of sugar</i>	<i>mgm.</i>
2	First	881.6	89.48
2	Second	480.8	45.32
2	Third	82.8	28.12
Total.....		1,445.2	162.92
4	First	1,100.0	139.92
4	Second	178.8	49.42
4	Third	30.0	20.52
Total.....		1,308.8	209.86

of the waxes, of the alcohol-soluble constituents, of the lignin-like, or what may be termed "lignin-humus," complexes, etc. For the present, however, it may be sufficient to limit the analyses to the aforementioned groups, to be able to bring out the differences in composition between the different kinds of peat and between peat and the plant materials from which it originated.

In the beginning of these studies, the hemicelluloses were obtained by boiling the material with 2 per cent HCl solution for 1 hour under the reflux condenser. It was soon found, however, that repeated extractions with fresh quantities of acid resulted in further extractions of hemicellulose and of nitrogen. Different results were obtained when a 4 per cent HCl slution was used instead of a 2 per cent solution, as shown in table 3. As far as the hemicelluloses are concerned, the 4 per cent acid solution presents no advantage over the more dilute acid and two extractions are sufficient to bring practically all the hemicellulose

into solution. It was later found that if the extraction is carried out under the reflux condenser a period of 5 to 6 hours is required, whereas at 15 pounds pressure in the autoclave, 1 hour is sufficient.

As far as the nitrogen made soluble by treatment with dilute acids is concerned, the more concentrated acid brings more of the insoluble nitrogen into solution, while even the third extraction yields almost half as much nitrogen as the second extraction. In view of the fact, however, that the maximum nitrogen figures (material soluble in dilute acids) do not represent any definite final group of complexes, the more prolonged extraction with the more concentrated acid was not carried out further.

One other phase of the method of analysis outlined here remains to be discussed, namely the results for the determinations of the lignin-like complexes. The assumption that all the organic matter that is not acted upon by concentrated acid (80 per cent sulfuric or 42 per cent hydrochloric) consists of

TABLE 4
"Lignin" and "humus" in peat
(On basis of original 10 gm. of dry peat)

	PRELIMINARY TREATMENT OF PEAT	2 PER CENT HCl (THREE TIMES)	4 PER CENT HCl (THREE TIMES)
Ash-free lignin	Total lignin.....mgm. Nitrogen in lignin.....mgm. Nitrogen in solution from lignin.....mgm.	4,992 133.52 69.66	4,772 119.58 34.93
Ash-free "Humus" content	Insoluble in 4 per cent NaOH solution...mgm. Nitrogen content of residue.....mgm. Precipitated "humus".....mgm. Nitrogen content of "humus".....mgm. Nitrogen content of solution from "humus".....mgm.	1,524 27.46 2,930 81.40 70.41	1,500 25.45 2,721 75.78 49.43

nothing but lignin, even if the nitrogen is accounted for, may be a little far fetched, especially since different solvents (alcohol, acetone, pyridine) will dissolve only a part of this lignin, and since it is known (31) that a part of the synthesized cell substance is also insoluble in the concentrated acids. Unfortunately, the alkali-lignin, or the lignin which is extracted with sodium hydroxide solution under pressure and precipitated with hydrochloric acid, does not represent any more the true lignin than the acid lignin, or that part of the plant material which is left unacted upon by strong acids. In accordance with the ideas of Bergius on the rôle of lignin in the origin of coal, we would expect that the alkali-lignin should form only a half of the acid lignin. This is usually the case, as found in various analyses on the lignin content of natural organic materials carried out in this laboratory.

The alkali-lignin corresponds exactly to the "humus" or "humic acids" found by the older chemists in organic matter which has undergone decomposi-

tion (soil, peat, manure, etc.). To throw some light on this problem and compare quantitatively the "lignin" and "humus" content of peat, the material left from the three treatments with 2 and 4 per cent hydrochloric acid (see table 3) was utilized. Out of 10 gm. of original dry peat, there was left, after 3 extractions with 2 per cent HCl, 6.456 gm. and, after 3 extractions with 4 per cent HCl, 5.925 gm. of residual material. These residues were now divided into several aliquot portions some of which were treated for 2 hours in the cold with 80 per cent sulfuric acid, then diluted with 15 volumes of water and autoclaved for 1 hour, and the lignin left determined. Other portions were extracted for 30 minutes at 1 atmosphere pressure with 4 per cent NaOH solution; this solution was filtered off and the residue was washed with 2 per cent acetic acid and water, then dried, weighed, and analyzed for nitrogen and ash; the "humus" was precipitated from the alkaline solution with hydrochloric acid, washed, dried, weighed, and analyzed for nitrogen and ash; the filtrate from the "humus" was also analyzed for nitrogen.

TABLE 5
"Lignin" and "humus" content in 2 layers of lowmoor peat
(Per cent of original dry, ash-free material)

FRACTION	I	II
Ether-soluble.....	1.27	1.06
Water-soluble.....	4.80	2.96
Soluble in 2 per cent HCl.....	28.08	25.50
Ash-free "lignin".....	52.63	61.79
"Humus" content.....	27.30	38.52
Residue not extracted with 4 per cent NaOH solution....	11.46	10.37

The results presented in table 4 show that nearly half of the original peat is present in the "lignin" fraction and that this fraction is nearly twice as large as the "humus" fraction in the peat. The concentration of the dilute acid used for the preliminary treatment does not influence appreciably either the "lignin" or the "humus" content of the peat. One would feel justified, from these results, in using the "lignin" figure rather than the "humus" in the peat analysis, since the yield of the former tends to approach a maximum, while the yield of the latter is a minimum and is, in addition, influenced by many factors, such as alkali concentration, nature of alkali, length and temperature of extraction, etc. Even when peat has been previously treated with dilute acids, in the extraction of "humus" with 4 per cent alkali solution under pressure, considerable quantities of nitrogen are lost in the form of ammonia.

Since the nitrogen is not considered an integral part of the lignin, but represents the "humin" form, or that part of the nitrogen which is not acted upon by hot dilute acids, the nitrogen found in lignin is multiplied by the arbitrary figure 6.25, and the product subtracted from the "lignin" residue to give pre-

sumably pure lignin. One must also keep in mind the fact that, in this particular experiment (recorded in tables 3 and 4), the peat was not extracted previously with ether and with alcohol, and the presence of these two fractions will tend to increase somewhat the "lignin" content of the material.

Table 5 presents further data for comparing the "lignin" content of peat with the "humus" content. The results were obtained from two samples of low-moor peat: fraction I was taken within the upper 10 to 15 cm. of the peat bog and still contains some undecomposed organic matter; fraction II was taken at a depth of 25-30 cm. from the surface. The ash content of fraction I was 20.3 per cent and of fraction II, 16.1 per cent. Fraction I contained 4.08 per cent nitrogen, on the dry basis, and fraction II, 3.60 per cent.

The samples were air-dried and treated with ether, water, and 2 per cent hydrochloric acid. Some aliquot portions were then treated with concentrated acid for the "lignin" determination, and some were extracted with 4 per cent NaOH solution to obtain the "humus" fraction. Here again we find that the yield of "humus" is only 50 to 60 per cent that of the "lignin."

The fact that the "lignin" fraction is quantitatively larger and qualitatively very promising for comparison with natural plant materials and also because the procedure for "lignin" determination is more definite and is easy to manipulate, enabling us to determine also the hemicellulose and cellulose fractions in the sample of material, the determination of "lignin" in peat should unquestionably take the place of the "humus" determination.

The authors do not wish to assume here that all the "lignin" found in peat is of exactly the same chemical nature as the lignin of higher plants. In view of the fact, however, that the chemistry of lignin in plants is still a matter of dispute and that the nature of the lignin varies with different plants, especially such plants as trees, grasses, and mosses, one may designate that fraction of the peat which is obtained by the same method of analysis as the lignin in plants by the term "peat lignin." Perhaps the terms "humus-lignin" or "modified lignin-humus complex" may prove to be more appropriate, since this lignin is known to consist partly of plant lignin, in a modified form, and partly of the so-called "humin" complexes, derived, not, as Marcusson and Bergius assume, from celluloses by chemical processes of hydrolysis and oxidation, but from celluloses and other carbohydrates and proteins through the activities of microorganisms. The exact chemical nature of this "humus lignin" will vary with the nature of the soil or bog in which it has been formed, depending upon the nature of the original plants, conditions under which the decomposition is taking place, and the microorganisms active in the process.

The results presented here show that the chemical composition, as obtained by a proximate analysis similar to one outlined above, can be used for the characterization of peat and can yield important information concerning its origin and the decomposition processes involved in its formation from plant materials. These data easily dispose of the assumption that the processes of peat formation are purely chemical in nature and that microbiological factors play no part in its formation.

Detailed studies of the chemistry of different peat profiles and the rôle of various groups of microorganisms in the decomposition of plant remains in peat bogs will be given in a later publication. In view of the fact that bacteria are probably largely the active agents in the decomposition processes in peat bogs (the fungi are active only upon the surface of the bog), and that bacteria—especially the cellulose-decomposing bacteria—as a rule prefer a less acid reaction, we would expect that the presence of calcium carbonate and available nitrogen, as in the case of the lowmoor and forest peats, would favor the processes of decomposition.

The complete absence of celluloses in the lowmoor peat throws a definite light upon the origin of these organic complexes. It has been pointed out

TABLE 6
Composition of some natural plant materials which give origin to peat
(On per cent basis of total dry matter)

PLANT MATERIAL	ETHER-SOLUBLE FRACTION	COLD- AND HOT-WATER SOLUBLE FRACTION	HEMICELLOSE	CELLULOSE	LIGNIN (ASH- AND NITROGEN-FREE)	PROTEIN	ASH	TOTAL
<i>Carex</i> -upper growing portion.....	2.54	12.56	18.36	28.20	21.08	7.08	3.30	93.12
<i>Carex</i> , rhizomes.....	1.66	3.18	20.86	11.78	41.74	14.62	4.56	98.40
<i>Cladidium</i> , upper growing portion..	1.14	6.87*	21.45†	28.31	29.09	7.19	3.89	97.94
<i>Cladidium</i> , lower portion and roots.	0.90	5.21*	20.75†	30.74	30.90	3.81	3.57	95.88
<i>Hypnum</i>	4.58	8.41	18.92	24.75	21.13	4.16	4.33	86.28
<i>Sphagnum</i> , upper growing portion	1.47	3.86*	30.82	21.13	6.97	5.88	3.18	73.31
<i>Sphagnum</i> , lower, dead portion...	1.60	1.56	24.50	15.88	19.15	1.86	19.92	84.47
Fallen needles of <i>Pinus strobus</i>	11.35	7.29	18.98	16.43	22.68	2.19	2.51	94.00
	(+12.57)‡							
Fallen oak leaves.....	4.01	15.32	15.60	17.18	29.66	3.47	4.68	89.92

* Cold water only.

† Pentosans only.

‡ Alcohol-soluble portion.

above that the older botanists and geologists as well as a number of modern chemists (36) put forth the claim that cellulose is the mother substance of peat and coal, while Fischer (5-7) and his associates brought definite evidence to show that lignins are the mother substances of these. The results presented here, especially when combined with the studies on the decomposition of natural plant materials under anaerobic conditions, tend to support Fischer's theory.

To interpret the results of peat analysis we must compare the chemical composition of the peat with that of the natural materials which gave origin to it. The proximate composition of a series of plant materials which are commonly found in peat formations is recorded in table 6. In addition to the

upper portion of the *Carex* plant, an analysis is also given of the rhizomes of *Carex*. The presence of considerable fungus mycelium in these rhizomes points to the fact that these have already been undergoing decomposition. This is found to hold true in the considerable reduction of the cellulose content and in the increase in the lignin and protein content.

The sphagnum moss contains large quantities of hemicelluloses which are hydrolyzed only on prolonged treatment with boiling dilute acids. There is a considerable discrepancy between the total loss in the moss constituents on boiling with the dilute acid and the amount of reducing sugars formed as a result of hydrolysis, showing that various substances which are not of a hemicellulose nature are brought into solution (organic acids, pectins, etc.). The amount of hemicellulose present, as calculated from the reducing sugars formed, is considerably larger than the pentosan content as determined directly on a separate portion, the young growing plants of *Sphagnum acutifolium* containing 30.82 per cent total hemicellulose and only 9.95 per cent pentosan. These discrepancies account for the fact that only 73.31 per cent of the young growing parts of the sphagnum is accounted for and 84.47 per cent of the dead portions of the plant.

When plants die, the constituents undergo various degrees of decomposition; the different chemical complexes do not all decompose with the same rapidity; while the different environmental conditions modify considerably the activities of microorganisms which bring about the processes of decomposition.

Under aerobic conditions all the plant constituents undergo transformations, some more rapidly, others more slowly. It was shown (34) for example, that as a result of the decomposition of mature rye straw within a period of 3 months at 25°C. in the presence of some additional nutrients (available nitrogen, phosphorus and potassium), 41.97 per cent of the total water-insoluble organic matter (ash-free) has disappeared (the water-soluble substances were decomposed even more rapidly). The residual 58 per cent of the organic matter included of course also some of the cell substance which had been synthesized by the microorganisms. A study of the transformation of the various chemical complexes of that organic matter is very illuminating: only 39.54 per cent of the pentosans and 44.17 per cent of the cellulose were left. In other words these polysaccharides decomposed much more rapidly than the total organic matter. On the other hand, 88.72 per cent of the lignin was left, and the final residue contained 2.87 times as much protein as was present originally in the undecomposed material. The low nitrogen content of the rye straw necessitated an assimilation of nitrogen from inorganic forms and a synthesis of microbial cell substances.

These three transformations; namely, the rapid decomposition of the pentosans and celluloses, the slow decomposition of the lignins, and the synthesis of microbial cell substance as measured by protein formation, can well be considered as the three leading processes in the decomposition of organic matter under aerobic conditions, as in the case of field and forest soils. Under these

conditions, lignins decompose, to be sure, much more slowly than the celluloses and hemicelluloses, but, if a long enough period of incubation is used, there will be found a marked reduction in the lignins.

Under anaerobic conditions, as in the case of peat bogs, the decomposition of organic matter proceeds in an entirely different manner from that which takes place under aerobic conditions. It has been shown elsewhere (35) that in the decomposition of 200 gm. of oak leaves in a medium saturated with water (anaerobic conditions) the hemicelluloses decreased in 12 months from 25.0 gm. to 12.81 gm. in the absence of CaCO_3 , and to 7.45 gm. in the presence of CaCO_3 ; under aerobic conditions, the reduction was from 25.0 gm. to 5.55 and 4.74 gm. respectively. The celluloses were reduced, under anaerobic conditions, from 31.84 gm. to 15.35 gm. in the absence of CaCO_3 , and to 14.95 gm. in the presence of CaCO_3 ; under aerobic conditions only 4.76 and 3.01 gm. of cellulose were left, respectively. The lignins were reduced, under anaerobic conditions, from 41.34 gm. to 39.35 gm. in the absence of CaCO_3 , and to 37.06 gm. in the presence of CaCO_3 ; under aerobic conditions, 26.25 and 22.48 gm. of lignin were left respectively. In other words, under anaerobic conditions practically all the lignin was left, while one-half of the cellulose and 60 per cent of the hemicellulose were decomposed. It is of interest to note that the organic nitrogenous complexes insoluble in water changed under anaerobic conditions from 18.4 to 16.7 per cent, and to 11.5 per cent under aerobic conditions.

We must also recognize the fact that there is a distinct difference in the composition of the plant materials which go to make up different peat bogs: 1. In lowmoor bogs, the plant associations consist of *Carex*, *Phragmites*, *Cladium*, etc., the residues of which are rich in lignins, but the polysaccharides, which are made up largely of celluloses and pentosans, undergo rapid decomposition in a medium which is rich in nitrogen and other mineral nutrients. 2. In highmoor peat bogs, species of *Sphagnum* predominate, which are low in lignin and in nitrogen but are rich in certain hemicelluloses; these undergo slow decomposition by certain limited groups of organisms, in a medium poor in nitrogen and available minerals.

Under anaerobic conditions which predominate in a peat bog, the plant proteins are rapidly decomposed. The true celluloses and the pentosans of the plant are also decomposed with a certain degree of rapidity. The lignins are very resistant and therefore will accumulate. Some of the hemicelluloses may decompose only very slowly, while the synthetic activities of the micro-organisms tend to increase both the hemicellulose and protein content of the residue.

SUMMARY

1. A method of proximate analysis, which accounts for about 90 per cent of the chemical constituents of peat, has been suggested.
2. By this method of analysis, we can readily differentiate between different kinds of peat materials.

3. This method of analysis enables us to determine the processes which have taken place in peat formation.

4. In lowmoor peat, the true celluloses have completely decomposed, while a part of hemicellulose is left, largely of a hexosan nature. The protein content is higher than in the original plant materials, because of the synthesizing activities of microorganisms which brought about the decomposition of the plant remains.

5. In highmoor peat, considerable quantities of both celluloses and hemicelluloses are left, showing that much less decomposition has taken place. The proteins are low because of the comparatively more rapid decomposition of the nitrogenous substances of the sphagnum plants than of the carbohydrates. Ether-soluble substances (waxes) have accumulated in the highmoor peat but not in the lowmoor peat.

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THE GROWTH OF COTTON IN VARIOUS NUTRIENT SOLUTIONS

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In a recent investigation which involved the utilization of different forms of plant-food by the cotton plant, very little information could be found in the literature available in regard to the suitability of various nutrient solutions for the growth of this crop. Consequently a study was made of several nutrient solutions as proposed by different investigators in order to determine which of these could be recommended for growing cotton in sand cultures under greenhouse conditions.

EXPERIMENTAL

The first experiment with the different nutrient solutions was started in the fall of 1926. The various nutrient solutions used and their composition as recommended by the different investigators are given in table 1. All of these solutions were used in the first study except the solution as recommended by Zinzandze (8), which was not added until 1927.

Glass percolators having a capacity of 1250 cc. were used in all of the following experiments. They were filled with white quartz sand, which was leached with distilled water to remove any soluble material present. Five cotton seeds were planted in each percolator. At the end of 10 days all but the two strongest plants in each percolator were removed. The different nutrient solutions were changed every $3\frac{1}{2}$ days, 500 cc. of distilled water being added to each percolator to displace the old nutrient solution before the fresh solution was added. The cotton plants which were supplied with the solution as recommended by Tottingham (7) for wheat seedlings began to show a superiority over the other plants at the end of 15 days and held this lead throughout the experiment, which lasted for 90 days. Two variations from the data given in table 1 occurred in this experiment. In the first case, rock phosphate instead of precipitated tricalcium phosphate was supplied in Crone's nutrient solution. The growth of the cotton plants in this solution was very poor. No conclusions, however, could be drawn in regard to the utilization of rock phosphate by cotton from this experiment because this solution might not have produced a good growth of cotton even though a different form of phosphate had been supplied. The second variation occurred in Knop's solution.

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TABLE I
The composition of nutrient solutions used by different investigators
 (Data are given as grams of salt for each liter of solution)

INVESTIGATOR	SALTS USED											
	CaCl ₂	Ca(NO ₃) ₂	Ca ₃ (PO ₄) ₂	CaSO ₄ ·2H ₂ O	FeCl ₃ ·6H ₂ O	FeSO ₄ ·7H ₂ O	KCl	K ₂ HPO ₄	KNO ₃	NaCl	NH ₄ NO ₃	(NH ₄) ₂ SO ₄
Cron (1)	0.560	0.250	0.500	Tr.	0.250	1.000	0.500
Hanssteen-Crammer (1)	1.000	0.800	0.500	Tr.	0.120	0.250	0.615	0.150	1.180
Knop (1)	0.800	1.724	0.853	2.363	0.500	0.500	0.100	0.200	0.200	0.200	0.200
Pfeiffer (2)	0.800	0.853	0.853	2.363	0.500	0.500	0.100	0.200	0.200	0.200	0.200
Sachs (1)	1.724	1.724	1.724	2.363	0.500	0.500	0.100	0.200	0.200	0.200	0.200
Schimper (4)	0.853	0.853	0.853	2.363	0.500	0.500	0.0044	0.0024	2.451	0.431	0.431	0.431
Shive (6)	0.853	0.853	0.853	2.363	0.500	0.500	0.0044	0.0024	1.770	0.495	0.495	0.495
Tottingham (7)	0.077	0.077	0.077	0.077	0.083	0.083	0.069	0.123	0.123	0.170	0.170	0.066
Zinzandze (8)	0.077	0.077	0.077	0.077	0.083	0.083	0.069	0.123	0.123	0.170	0.170	0.066

Potassium nitrate was accidentally added to this solution instead of calcium nitrate. This error was not detected until after the experiment was started, consequently the correction could not be made in this test. It is interesting to note, however, that the cotton plants always appeared very healthy in this solution which contained no calcium, although their growth was somewhat stunted.

There was very little difference in the growth of any of the plants in percolators which received the same nutrient solution. At the end of 7 weeks, one series of plants grown in the different nutrient solutions was removed from the percolators, measured, photographed, and then dried and weighed. The cotton in the other series was allowed to grow for 90 days before it was removed. Plate 1, figure 1, shows the cotton plants grown in the first experiment at the end of the 90-day period. Very little difference in the rate of development of the plants occurred between the 49- and 90-day periods, consequently only one photograph is shown.

TABLE 2
Height and weight of cotton plants grown in different nutrient solutions

SOLUTION USED	pH OF SOLUTION	HARVESTED 49 DAYS AFTER PLANTING		HARVESTED 90 DAYS AFTER PLANTING	
		Height inches	Dry weight of tops and roots gm.	Height inches	Dry weight of tops and roots gm.
Tottingham.....	5.1	10.50	3.52	12.60	13.88
Shive.....	5.3	7.75	2.28	11.40	10.76
Pfeffer.....	5.2	8.00	2.20	9.00	7.40
Sachs.....	5.7	6.25	1.75	9.00	6.43
Hansteen-Cranner.....	5.3	9.00	1.93	11.60	6.31
Schimper.....	5.7	8.50	1.75	14.00	5.50
Knop.....	6.1	6.75	1.72	8.60	5.86
Crone.....	5.7	5.50	1.08	8.40	3.69
Distilled water.....	...	3.50	0.52	3.50	1.04

The measurements and the dry weights of the plants at the two different stages of development are given in table 2. The data on height are the averages of the two plants grown in each percolator. The weights include the tops and roots after being dried overnight at 105°C.

Some of the plants showed considerable chlorosis in this experiment, notably in Schimper's and Hansteen-Cranner's solutions. It will be noted from the photograph that the plants in these percolators lost their lower leaves rapidly. This affected their total weight considerably when the final weights were secured. Some chlorosis appeared on the leaves of the cotton plants grown in the sand cultures containing Knop's and also Sach's solution but none appeared in any of the other solutions.

This experiment was repeated in the greenhouse in the spring of 1927 but because of unfavorable temperatures and insect injury, the results were not

reliable, consequently the data were not included in this report. Tottingham's and Shive's solutions again produced a more vigorous growth than any of the other solutions used. Studies on Tottingham's solution diluted to one-tenth of the original concentration did not give as good growth as Pfeffer's solution undiluted.

In order to check the results secured in this experiment, another experiment was started in the fall of 1927 using the same solutions as given in table 2 with the addition of another solution recommended by Zinzandze (8) for maize. In

TABLE 3

Dry weight and average height of cotton plants grown in sand culture to which various nutrient solutions were added

SOLUTION USED	pH VALUE	AVERAGE HEIGHT <i>inches</i>	AVERAGE GREEN WEIGHT		AVERAGE DRY WEIGHT	
			Tops	Roots	Tops	Roots
Shive.....	5.3	11.25	28.50	9.50	5.86	1.36
Tottingham.....	5.3	10.50	27.75	11.50	5.07	1.78
Schimper.....	5.7	10.50	20.75	11.75	4.42	1.87
Pfeffer.....	5.7	8.00	13.00	8.50	2.62	1.13
Zinzandze.....	6.00	8.50	10.75	7.25	2.60	1.23
Hansteen-Cranner.....	5.4	10.00	17.00*	8.00	2.35	1.39
Sachs.....	6.4	7.40	9.75	5.25	1.64	1.01
Crone.....	6.9	6.25	7.00	6.00	1.62	0.77
Distilled water.....	3.25	2.00	1.75	0.61	0.41

* Not duplicated.

TABLE 4

Data on the growth of cotton in sand culture when supplied with Pfeffer's nutrient solution containing monopotassium phosphate and in Pfeffer's solution in which finely ground rock phosphate is substituted for the monopotassium phosphate

PFEFFER'S SOLUTION	pH VALUE	HEIGHT OF PLANTS <i>inches</i>	GREEN WEIGHT OF TOPS AND ROOTS	DRY WEIGHT OF TOPS AND ROOTS	PER CENT OF PO_4 IN PLANTS
			<i>gm.</i>	<i>gm.</i>	
Phosphorus as KH_2PO_4	5.7	8.0	21.5	3.75	0.146
Phosphorus as Rock Phosphate.....	6.2	6.0	11.5	2.42	0.073

the first experiment all the salts that were used were recrystallized before the solutions were prepared. In this experiment "chemically pure" salts were used as they came from the manufacturer. The pH values of the solutions were higher than in the previous test and also for some unexplainable reason the cotton seed failed to germinate in the sand cultures containing Knop's solution. Also only two plants survived in one of the percolators treated with Hansteen-Cranner's solution. As a result of this unfortunate occurrence an accurate comparison of the value of Knop's solution cannot be made as an error occurred in making it up in the first experiment.

The data for the last experiment are given in table 3. On two different occasions the temperature in the greenhouse dropped so low that the cotton plants were chilled and the growth at the end of the experiment was considerably less than that secured in 1926. This difference may be explained partially by a difference in the intensity of the light in the two experiments, since the percolators were located on the north bench of the greenhouse in this experiment and did not receive as much light as the plants grown in the first experiment which were located on the south bench.

One of the duplicates in the sand culture treated with Shive's nutrient solution produced an exceptionally large plant in the last experiment and this is the reason why this solution produced a larger amount of dry matter than Tottingham's solution. The leaves of the plants grown in Shive's solution showed considerable chlorosis in this experiment. A photograph of this condition is shown in plate 1, figure 2. No chlorosis appeared in Shive's solution in the first experiment although the leaves were a much lighter green than those of the plants grown in Pfeffer's and in Tottingham's solutions. Just the reverse condition occurred in the case of Schimper's solution, which produced

TABLE 5

Iron content of plants grown in various nutrient solutions to which different amounts of iron salts were added

SOLUTION USED	DRY WEIGHT OF PLANT	WEIGHT OF ASH	Fe in Plant	
			mgm.	per cent
Crone.....	1.28	0.178	0.48	0.0375
Sachs.....	1.79	0.308	0.40	0.0223
Zinzandze.....	2.82	0.309	0.60	0.0212

considerable chlorosis in the first experiment when the salts were all recrystallized but produced none in the last experiment when the ordinary laboratory reagents were used in preparing the nutrient solutions.

The plants grown in Hansteen-Cranner's solution were very succulent when harvested and produced less dry matter than other plants having considerably less green weight.

A study of the utilization of rock phosphate by cotton plants was also included in this experiment. Pfeffer's solution was used for this study because of its lower salt concentration than either Shive's or Tottingham's solutions. Although it did not produce as large a growth of cotton as either of the other solutions, the plants fruited normally, and, therefore, since the pH of the solutions used by Tottingham and Shive cannot be increased without the formation of a precipitate, the solution as used by Pfeffer was preferred.

The data on the utilization of rock phosphate by cotton when substituted for monopotassium phosphate in Pfeffer's nutrient solution are given in table 4 and a photograph of the plants is shown in plate 1, figure 3. The phosphorus content of these plants is also included. The percentages of phosphorus are

considerably lower than those given by Fraps (3) and by McHargue (5), but the comparison shows that in sand culture cotton plants do not absorb as much phosphorus from rock phosphate as they do when the phosphorus is present in a more soluble form. Why there should be such a wide variation in the phosphorus content of plants grown in the field and in nutrient solutions containing an excess of water-soluble phosphate cannot be explained at this time.

Crone's nutrient solution did not produce a satisfactory growth of cotton even when precipitated tricalcium phosphate was used. Soluble ferric phosphate was added to all the solutions in the last experiment and as Crone's solution requires a large amount of ferric phosphate, it was suggested that an excess of iron might be causing the stunted development. In order to determine whether there was an excessive amount of iron present in the plants grown in solutions containing large amounts of iron salts, the plants grown in the sand cultures treated with Crone's Zinzandze's and Sachs' nutrient solutions were analyzed. The data are given in table 5.

Although the amount of soluble iron added in Zinzandze's solution was much greater than in the other solutions, much of it hydrolyzed and precipitated as ferric hydroxide. According to the variation of the iron content in other plants it would appear that this element has not been the limiting factor in the growth of these plants.

An attempt was made to grow cotton in solutions of varying pH values but on account of the difficulty in preventing the formation of a precipitate, which would change the salt concentration, this phase of the investigation was not completed. Since cotton makes a very satisfactory growth on the basic soils of western Oklahoma and Texas and also grows luxuriantly on the acid soils in the Southeastern states when sufficient plant-food is present in the soil, there is little doubt that the cotton plant has a wide range of adaptation with reference to soil reaction.

SUMMARY

A study was made of the growth of cotton plants in sand cultures to which various nutrient solutions were added.

Nine different nutrient solutions were included in this investigation. In three different tests Tottingham's solution produced the most satisfactory growth of cotton although in one instance Shive's solution produced a slightly larger plant but did not produce a normal development of squares and bolls.

Pfeffer's nutrient solution produced a very satisfactory growth of cotton and because of its lower salt concentration may be preferable under certain conditions to either Tottingham's or Shive's nutrient solution.

The utilization of rock phosphate by the cotton plant was very poor when substituted for monopotassium phosphate in Pfeffer's nutrient solution, even though a considerable amount of insoluble phosphate was transferred to the sand culture when the solution was added. Since the absorption of iron by the cotton plants grown in different nutrient solutions was not in proportion

to the amount of iron present in the nutrient solution, an excessive amount of iron in Crone's nutrient solution does not explain the poor growth of cotton produced by that solution.

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PLATE 1

FIG. 1. Growth of cotton plants in sand cultures to which various nutrient solutions were added as given in table 1. 1, Crone; 2, Shive; 3, Schimper; 4, Tottingham; 5, Sachs; 6, Hansteen-Cranner; 7, Knop; 8, Pfeffer.

FIG. 2. Chlorosis of cotton plants grown in Shive's nutrient solution (left) as compared with Schimper's solution (right).

FIG. 3. Utilization of phosphate by cotton plants. Pfeffer's nutrient solution containing KH_2PO_4 on the left and same solution containing rock phosphate in the center; cotton plants grown in Tottingham's solution shown on the right.



FIG. 1



FIG. 2



FIG. 3

VARIATIONS IN THE MANGANESE CONTENT OF CERTAIN VEGETABLES¹

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For many years control and research laboratories have been accumulating a vast amount of data on the carbohydrate, fat, and protein content of our food-stuffs. No such body of information exists with respect to the mineral elements in foods. We need to know the facts concerning the mineral elements, and we need also to obtain such data from a number of widely separated sources because of the great variations which exist in the mineral content of different samples of the same foodstuff. An immense amount of analytical data from laboratories in different parts of the United States must be accumulated before we can even approximate the average mineral composition of our food materials. Such data should cover not only the major mineral elements, calcium, phosphorus, iron, but also those occurring in minor quantities, iodine, copper, zinc, manganese, etc. On the basis of the present available data, it is unsafe to draw any definite conclusion as to the adequacy of particular diets with respect to the mineral elements.

In a previous paper (1) the manganese content of 84 samples of our principal food materials was given. Samples of a few of these materials were available in considerable number. As these samples had been grown on different types of soil it was decided to analyze all of them in order to learn what variations existed.

EXPERIMENTAL

The procedure followed in the preparation and analysis of the samples was the same as that given in an earlier publication (1).

In tables 1, 2 and 3 are given the chief facts describing the samples and their manganese content. Many of these samples have already been analyzed for calcium, iron, and phosphorus (2, 3).

Manganese in cabbage

In the 22 samples of cabbage, the manganese ranged from 0.00052 to 0.00159 per cent. This variation does not appear to be connected with the type of

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soil on which the cabbage was grown. Samples grown on contrasting types of soil showed no greater variations than those that existed among samples grown on the same kind of soil. The largest number of samples grown on a single type of soil was from silt loams; these samples varied from 0.00082 to 0.00159 per cent and averaged 0.00109 per cent. The samples from an entirely differ-

TABLE 1
Manganese content of cabbage

NUM-BER	VARIETY	SOURCE	SOIL TYPE	DATE OF HARVEST	MAN-GANESE IN SAMPLE, DRY BASIS*
				1924	mgm. per kgm.
318	Copenhagen	Fremont, O.		August 21	8.9
322	Copenhagen	Fremont, O.	Fine sandy loam	September 17	11.1
324	Hendrickson Early	Madison, Wis.	Marsh	September 29	9.3
325	Hendrickson Early	Madison, Wis.	Marsh	September 29	10.0
326	All Seasons	Wichert, Ill.		October 1	15.3
328	Copenhagen	Franksville, Wis.	Well decomposed peat	October 4	5.2
329	All Seasons	New London, Wis.	Silt loam	October 7	9.7
330	Copenhagen	New London, Wis.	Silt loam	October 8	8.9
331	Succession	New London, Wis.	Silt loam	October 8	8.8
332	All Seasons	Clyde, O.	Sandy loam	October 10	10.0
333	All Seasons	Madison, Wis.	Marsh	October 24	9.0
334	Copenhagen	Phelps, N. Y.	Silt loam	October 21	15.9
336	All Seasons	Bellevue, O.	Silt loam	October 28	8.2
337	Holland	Franksville, Wis.		November 9	9.0
338	All Seasons	Franksville, Wis.		November 9	9.1
339	All Seasons	Phelps, N. Y.	Silt loam	November 12	14.3
340	All Seasons	Madison, Wis.	Marsh	November 25	15.0
341	Succession	New London, Wis.		December 1	8.9
				1925	
349	All Seasons	Madison, Wis.	Alkaline marsh	September 29	12.5
350	All Seasons	Madison, Wis.	Miami silt loam	October 6	13.4
352	All Seasons	Madison, Wis.	Alkaline marsh	October 23	9.1
354	All Seasons	Madison, Wis.	Miami silt loam	October 28	11.1
Average.....					10.6

* The average moisture content of the 22 samples of cabbage was 92.8 per cent.

ent type, the marsh soils, varied somewhat more widely from 0.00052 to 0.00150 per cent, but averaged 0.00101 per cent, almost the same as those from the loams.

Variety or date of harvest does not influence to any marked extent the manganese content of the cabbage. The average manganese content of the Copen-

hagen samples was 0.00100 per cent, while that of the All Seasons was 0.00114 per cent. The average manganese content of the samples harvested prior to October 11, was 0.00103 per cent, whereas that of those harvested after October 11 was 0.00110 per cent.

Manganese in green peas

In the 13 samples of peas the manganese ranged from 0.00098 to 0.00252 per cent with an average of 0.00157 per cent. The soils represented by these

TABLE 2
Manganese content of green peas

NUM-BER	VARIETY	SOURCE	SOIL TYPE	SIZE	MAN-
					GANESE
					per kgm.
10	Alaska	Cobb, Wis.	Carrington silt loam	2	19.6
22	Alaska	Beaver Dam, Wis.	Miami silt loam	2	25.2
31	Alaska	Lodi, Wis.	Miami silt loam	3	10.3
38	Alaska	Augusta, Wis.	Boone fine sandy loam	2	22.5
46	Alaska	Horicon, Wis.	Miami silt loam	2	11.1
70	Perfection	Cobb, Wis.	Carrington silt loam	3	9.8
72	Perfection	Cobb, Wis.	Carrington silt loam	5	10.8
81	Perfection	Templeton, Wis.	Miami silt loam	3	22.5
83	Perfection	Templeton, Wis.	Miami silt loam	5	17.0
90	Horsford's Garden	Market	Plymouth, Wis.	Miami silt loam	1 and 2
92	Horsford's Garden	Market	Plymouth, Wis.	Miami silt loam	4
101	Horsford's Garden	Market	Gillett, Wis.	Miami fine sandy loam	3
103	Horsford's Garden	Market	Gillett, Wis.	Miami fine sandy loam	5
<i>Average.....</i>					15.7

* The average moisture content of the 13 samples of peas was 79.4 per cent.

samples are all loams, but the peas grown on these soils varied greatly in their content of manganese. For example, although samples 22 and 46 were both grown on Miami silt loam, no. 22 contained twice as much manganese as no. 46.

Variety seems to have little effect on the manganese content. The early variety, Alaska, covers about the same range as the two late or wrinkled varieties, Perfection and Horsford. The averages for the three varieties are 0.00177, 0.00150, and 0.00138 per cent, respectively.

Size does not affect the manganese content in any uniform manner, as can be seen by comparing the following pairs of samples: 70 and 72, 81 and 83, 90 and 92, and 101 and 103. The samples in each pair were obtained from the same vines. All the pods on the vines were picked at the same time, the peas were shelled and then graded with sieves into the sizes recognized in commercial canning. Only one of the above pairs of samples, 81 and 83, shows any marked difference in the manganese content of the two sizes. In this pair the

TABLE 3
Manganese content of string beans

NUM-BER	VARIETY	SOURCE	SOIL TYPE	SIZE	MAN-GANESE IN SAMPLE, DRY BASIS*
					mgm. per kgm.
243	Wardwell's Wax	Shawano, Wis.	Plainfield sand	All	45.8
244	Refugee Wax	Shawano, Wis.	Plainfield sand	All	43.8
245	Full Measure	Shawano, Wis.	Plainfield sand	All	57.0
248	Giant Stringless Green	Evansville, Wis.	Carrington silt loam	All	38.3
254	Full Measure	Evansville, Wis.	Carrington silt loam	All	35.9
255	Wardwell's Wax	Evansville, Wis.	Carrington silt loam	All	38.7
261	Refugee Green	Argyle, Wis.	Kennan silt loam	All	33.6
281	Refugee Green	Chetek, Wis.	Colby silt loam	All	35.8
287	Refugee Wax	Gillett, Wis.	Miami silt loam	All	29.6
293	Imperial Kidney Wax	Gillett, Wis.	Miami silt loam	3	33.2
295	Imperial Kidney Wax	Gillett, Wis.	Miami silt loam	5	33.3
297	Imperial Kidney Wax	Gillett, Wis.	Miami silt loam	All	51.3
304	Refugee Green	Madison, Wis.	Miami gravelly sandy loam	All	22.1
308	Refugee Green	Niellsville, Wis.	Boone fine sandy loam	3	43.4
310	Refugee Green	Niellsville, Wis.	Boone fine sandy loam	5	44.1
339	Refugee Wax	Spring Green, Wis.	Plainfield sand	3	52.8
341	Refugee Wax	Spring Green, Wis.	Plainfield sand	4	44.4
440	Refugee Green	Spring Green, Wis.	Plainfield sand	3	30.2
<i>Average.....</i>					39.6

* The average moisture content of all the samples was 91.4 per cent.

smaller size contains considerably more manganese than the larger size. In another pair, samples 70 and 72, the relations are reversed.

Manganese in string beans

Like the cabbage and pea samples, the beans showed wide variations in their manganese content. For example, no. 245 contains about two and one-half times as much manganese as no. 304. Samples grown on the same type of soil also varied greatly in percentage of manganese. The four samples of

Refugee Wax beans averaged about 20 per cent more manganese than the six samples of Refugee Green. That this is a constant varietal difference can not be concluded, however, from such a limited number of samples.

Manganese in tomatoes

Four samples of tomatoes were found to vary from 0.00111 to 0.00191 per cent and averaged 0.00152 per cent. On the dry basis the average figure is about the same as that for green peas. On the fresh basis the green peas contained approximately 3 times as much manganese as the tomatoes.

SUMMARY

The manganese in 22 samples of cabbage, 13 samples of green peas, 18 samples of string beans, and 4 samples of tomatoes has been determined. On the fresh basis the average is as follows: cabbage 0.000076 per cent, green peas 0.00032 per cent, string beans 0.00034 per cent, and tomatoes 0.000091 per cent. Variations of from 200 to 300 per cent were found among the samples of each class of vegetable. These variations do not appear to be correlated with the type of soil on which the samples were grown. They are probably related to the amount of available manganese in the soil rather than to the type of soil.

No clearly defined relation seems to exist between the manganese content and the variety, size, or date of harvest of the vegetable.

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COMPOSITION OF NATURAL ORGANIC MATERIALS AND THEIR DECOMPOSITION IN THE SOIL: III. THE INFLUENCE OF NATURE OF PLANT UPON THE RAPIDITY OF ITS DECOMPOSITION

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It has been shown in a previous contribution (9) that in the study of decomposition of plant materials it is quite essential that we know the proximate composition of these materials, before we are able to account for the rapidity of their decomposition and the liberation of the various nutrients, especially of the element nitrogen, in forms available to plants. Such information is of great importance for the understanding of the practice of green manuring, of composting of stable manures, the preparation of artificial manure from plant residues, and the decomposition of organic matter in nature in general.

A method of proximate analysis has been proposed, which accounts for 90 or more per cent of the plant constituents, in terms of definite chemical complexes. This method has since been considerably modified in further investigations, especially when applied to the analysis of the organic material which has already undergone decomposition, or in the analysis of soil material, which is largely organic in nature, such as forest (11) and peat (8) soils. It was found desirable to use the same modified procedure for the analysis of both undecomposed plant material and of decomposed residues. This modified method has been used, therefore, with great advantage in the investigations reported here.

It was found previously (10) that when a comparison is made of the rapidity of decomposition of a plant which has been harvested at different stages of growth, different results are obtained. The more mature the plant is the less readily does it decompose. Whereas the decomposition of the young plant results in a rapid liberation of nitrogen, the decomposition of the same plant at a more mature stage requires the addition of an outside source of inorganic nitrogen before it can proceed to any extent. The reasons for this are brought out by a careful analysis of the constituents of the plant at the different stages of growth.

This analysis showed that a third of all the constituents of the young rye plant, on a dry basis, consisted of water-dissoluble substances, including considerable quantities of sugars and amino acids. The young plant contained,

¹ The authors are indebted to Mr. K. R. Stevens of this laboratory for assistance in carrying out some of the analyses.

on a dry basis, 2.5 per cent nitrogen, 7.7 per cent ash, 16.6 per cent pentosan, 18.06 per cent cellulose, and 9.9 per cent lignin. With the advance in the age of the plant, there was a rapid decrease in the nitrogen content and in the fat and ash content and a gradual increase in the cellulose, pentosan, and lignin content. There was a considerable decrease in the amount of water-soluble constituents. The mature plant (exclusive of the grain and roots) contained 0.24 per cent nitrogen, 22.9 per cent pentosan, 36.3 per cent cellulose, 19.8 per cent lignin, and 9.9 per cent water-soluble substances.

Similar results were obtained by Beckmann, Liesche and Lehmann (2), who did not analyze the very young plants however. Particular emphasis was laid upon the increase in the lignin content with the increase in the maturity of the plant. The lignin of mature rye straw was reported as 20.49 per cent, when determined by the Wilstätter method, and 18.12 per cent when measured by alkali extraction. The methoxyl content of the lignin also increased with the age of the plant, reaching 13.42 per cent at maturity.

Not only the composition of Gramineae but also that of Leguminosae (6) and even of leaves and needles of trees varies with the age of the plant (3). As a result of a detailed analysis of a number of data on the decomposition of plant and animal residue, using nitrate formation in soil as an index of the rapidity of decomposition, Whiting (12) came to the conclusion that the water-soluble nitrogen content of the material determines largely the rate of nitrate formation in the initial periods of decomposition. A high content of total nitrogen is usually accompanied by a high content of water-soluble nitrogen and leads to rapid nitrate formation. This is probably the reason why the decomposition of legumes leads to more rapid nitrate formation than the decomposition of non-legumes, and of young plants more rapidly than of old plants of the same kind. Whiting and Richmond (13) have shown further that the high water-soluble nitrogen may be a more important factor in the rapid formation of nitrates in the decomposition of plants than the total nitrogen content. This was illustrated by the various parts of the biennial white sweet clover, the roots of which, although containing less total nitrogen than the leaves but more water-soluble nitrogen, nitrified more rapidly than the leaves.

When the decomposition of the same plant at different stages of growth is determined, any differences found in the rapidity of decomposition and in the liberation of available nitrogen can thus be fully accounted for by the differences in the composition of the plant. Of prime importance in this connection, are the amount of water-soluble substances, of total nitrogen, of total cellulose and hemicellulose, and the lignin, fat, and wax content.

There may be a difference, however, between the nature of the plant constituents in different plants. In other words, our knowledge of the chemistry of the different plant constituents may be insufficient as yet to account for certain differences in the rate of decomposition of different plants.

Bal (1) has shown that when nitrate formation is used as an index of the decomposition of green manure in the soil, certain plants will be-

have differently from others. In the case of the sann-hemp (*Crotalaria juncea*), the earlier the plant is used as a green manure the more rapid is its decomposition. In the case of dhainca (*Sesbania aculeata*), however, there was no marked decrease in the rate of nitrification with an increase in the age of the plant used as a green manure. When the evolution of CO₂ was used as index of decomposition, the differences in the behavior of the two plants can be readily explained by the fact that the dhainca has made a much slower growth, and contained more nitrogen in relation to carbon (narrower carbon-nitrogen ratio) than the sann hemp. This was true especially of the latter stages of growth when this ratio became considerably wider in the sann hemp than in the dhainca. Even in these experiments, one can show that the differences in the rapidity of decomposition of different plants, as measured either by the evolution of carbon dioxide or by the liberation of available nitrogen, can be explained by the differences in plant composition. The nitrogen which is liberated as ammonia is soon changed, especially in soil, to nitrates.

The following investigations were undertaken with the idea of establishing: first, how differences in the composition of different plants influence the decomposition processes and, secondly, how these can be modified by the addition of available nutrients to the plant material.

For these studies a series of plant materials were selected to give as large a variety of plant types as possible and to give a marked variation in composition, not only from a quantitative point of view, but also qualitatively, i.e. in the nature of the constituents. These included: rye straw harvested as hay when nearly mature; corn stalks, including the leaves of the corn plant, harvested when the plant was already mature; oak leaves collected from the tree when they were fully mature and brown; alfalfa tops, including the stems and leaves harvested during the growing stage in the field, late in the summer; pine needles collected from surface of the ground soon after they had fallen from the tree; two mosses, one a mixture of sphagnum plants, largely *S. acutifolium*, including the living and the upper dead portions, and the other *Leucobryum*, carefully divided into the living and dead portions of the plant.

These materials were air-dried and used in the ground form for analysis and for the study of decomposition, with the exception of the *Sphagnum* and the *Leucobryum*, which were used in the ground form for the analyses only.

Sufficient material was placed in a series of 300-cc. round-bottomed, long-necked flasks (7), to give 5 gm. of dry matter. Distilled water was added to bring the moisture to 200 per cent on a dry basis, except in the case of the mosses, which received 500 per cent moisture. Some of the flasks received nutrients in the form of 200 mgm. of (NH₄)₂HPO₄ and 100 mgm. K₂HPO₄. A suspension of a good field soil was used for the inoculation of all of the flasks. These were now placed in a thermostat, kept at 25–27°C., and connected with an aeration apparatus to determine the evolution of carbon dioxide during decomposition. Decomposition was allowed to proceed for 28 days, without disturbing the material.

At the end of the decomposition period, the residues were treated with cold water to extract the water-soluble substances, then with a 4 per cent KCl solution to remove all the remaining ammonia. Ammonia and soluble organic matter were determined in the extracts. The residual material was washed with water, dried, weighed, and then used for the determination of hemicellulose, cellulose, and lignin.

Although no complete analysis has been made of the material left at the end of the decomposition period, a detailed analysis of the original plant substances is given in table 1, to enable one to compare the influence of the composition upon the rapidity and rate of decomposition.

The methods of analysis outlined previously (9) have been modified in several respects for the sake of greater simplification and for the purpose of

TABLE 1
Composition of original plant materials
(On per cent basis of dry material)

PLANT MATERIAL	RYE STRAW	CORN STALKS	DEAD OAK LEAVES	ALFALFA TOPS	SPHAGNUM	DEAD NEEDLES OF PINUS STROBIFOLIA
Ash content.....	4.18	7.54	5.10	10.30	5.01	2.51
Ether-soluble portion.....	1.83	1.75	3.85	2.75	1.11	11.37
Cold-water-soluble organic matter.....	4.51	10.58	8.28	12.44	3.07	4.42
(Sugar).....	(0.882)	(6.00)	(2.73)	(1.31)
Hot-water-soluble organic matter.....	1.75	3.56	5.73	4.80	3.88	2.86
Alcohol-soluble organic matter*.....	3.49	4.19	5.92	7.66	2.68	12.58
Hemicellulose.....	24.82	21.91	17.97	13.14	27.73	17.10
Cellulose.....	33.92	28.67	12.78	23.65	19.21	14.79
Lignin.....	12.44	9.46	24.76	8.95	7.33	21.89
Crude protein†.....	0.94	2.44	4.25	12.81	5.50	2.12
Total accounted for.....	87.88	90.10	88.64	96.50	75.52	89.64

* This was carried out on separate portions following ether extraction.

† This figure is obtained by multiplying the difference between the total- and cold-water-soluble nitrogen by 6.25.

enabling the analyst to carry out a complete analysis (except for the ash and total nitrogen) on a 5 or even a 3-gm. sample of material.

In the modified method of analysis (8), the material is extracted with ether, with cold water, and with hot water, in turn, and the extracts are analyzed according to the previous methods (soluble organic matter, soluble nitrogen, and reducing sugars). The residue is then treated on a water bath for 1 hour with hot 95 per cent alcohol; the combined filtrate and washings are evaporated and the soluble material is determined. The dried and weighed residue is removed carefully from the paper and boiled with 100 cc. of a 2 per cent solution of hydrochloric acid for 5 hours under a reflux condenser. This treatment results in the hydrolysis of the hemicelluloses, with the formation of reducing sugars. By determining these, one can readily calculate (multiplying

by 0.9) the hemicellulose content of the preparation. Boiling at ordinary atmospheric pressure with dilute acid has only a slight effect upon the cellulose, but results in the complete hydrolysis of the hemicelluloses; prolonged boiling is essential to get the maximum amount of reducing sugar. The amount of hemicellulose thus obtained is always larger, and often considerably larger than the pentosan content of the material obtained by the phloroglucide

TABLE 2
Composition and decomposition of rye straw
(On the basis of original 5 gm. of dry material)

CONSTITUENT GROUPS	ORIGINAL MATERIAL	DECOMPOSED MATERIAL	
		No nutrients	Nutrients added
Cold-water-soluble organic matter.....	226	80	130
Water-insoluble organic matter.....	4,565	4,380	3,289
Hemicellulose.....	1,241	1,132	615
Cellulose.....	1,696	1,649	964
Lignin.....	622	580	565
Carbon given off as CO ₂ in the process of decomposition.....	165.9	584.6
Ammonia-nitrogen used up.....	0	33.9

TABLE 3
Composition and decomposition of corn stalks
(On the basis of original 5 gm. of dry material)

CONSTITUENT GROUPS	ORIGINAL MATERIAL	DECOMPOSED MATERIAL	
		No nutrients	Nutrients added
Cold water-soluble organic matter.....	529	160	190
Water-insoluble organic matter.....	4,094	3,378	2,447
Hemicellulose.....	1,096	703	363
Cellulose.....	1,434	1,019	551
Lignin.....	473	468	422
Mgm. of carbon given off as CO ₂	500.7	870.4
Nitrogen used up as ammonia.....	0	30.8

method. This is due to the presence of various hexosans, such as galactans, mannans, and glucosans in the plant substances.

A definite portion of the residue left after the treatment of the material with dilute acid is now placed in a 500-cc. flask or beaker and to this is added 10 times as much (by volume) of 80 per cent sulfuric acid solution (usually 10 cc. acid to 1 gm. of dry material) which is allowed to act for 2 hours at room temperature. The acid is then diluted with 15 volumes of water and the solu-

tion boiled for 5 hours under a reflux condenser, or autoclaved for 1 hour at 120°C.

The filtered extract contains the glucose which has been produced quantitatively from the cellulose, and the residue contains the lignin. By determining the reducing sugar in the extract one can calculate (multiplying by 0.9) the cellulose content of the material. The lignin is determined from the residue by subtracting the ash content and the "humin" content (total nitrogen \times 6.25).

TABLE 4
Composition and decomposition of alfalfa plant
(On the basis of original 5 gm. of dry material)

CONSTITUENT GROUPS	ORIGINAL MATERIAL		DECOMPOSED MATERIAL
	mgm.	mgm.	mgm.
Cold-water-soluble organic matter.....	622		334
Water-insoluble organic matter.....	3,867		2,738
Hemicellulose.....	657		280
Cellulose.....	1,183		882
Lignin.....	448		486
Carbon given off as CO ₂		718.4
Nitrogen liberated as ammonia.....		24.2

TABLE 5
Composition and decomposition of oak leaves
(On the basis of original 5 gm. of dry material)

CONSTITUENT GROUPS	ORIGINAL MATERIAL	DECOMPOSED MATERIAL	
		No nutrients	Nutrients added
Cold-water-soluble organic matter.....	414	92	138
Water-insoluble organic matter.....	4,331	4,206	3,873
Hemicellulose.....	899	665	495
Cellulose.....	639	544	465
Lignin.....	1,238	1,211	1,208
Carbon given off as CO ₂	193.2	327.0
Nitrogen used up as ammonia.....	0	20.2

By this method of procedure, which simplifies considerably the manipulations as compared with those outlined previously, the analyses of the fresh plant material and of the decomposed residues can be carried out rapidly and with a high degree of accuracy. The method is especially valuable since it can be used for the analysis of peats, forest soil, and other organic formations, as has been shown elsewhere (11). By this method, 88 to 97 per cent of the plant constituents are accounted for, except in the case of the mosses. The presence of considerable quantities of organic acids, pectins, gums, and similar substances, which are not accounted for in the methods used, reduced the sum total of the products considerably.

To prove that this is the case, one need only compare the total organic matter soluble in hot dilute acid with the reducing sugar formed. After the moss has been treated with ether, water and alcohol, the dilute acid treatment may remove 50 to 55 per cent of the total dry material, but the amount of reducing sugar formed is only about 30 per cent, which gives 27 per cent hemicellulose. It is the difference between these two sets of figures that accounts

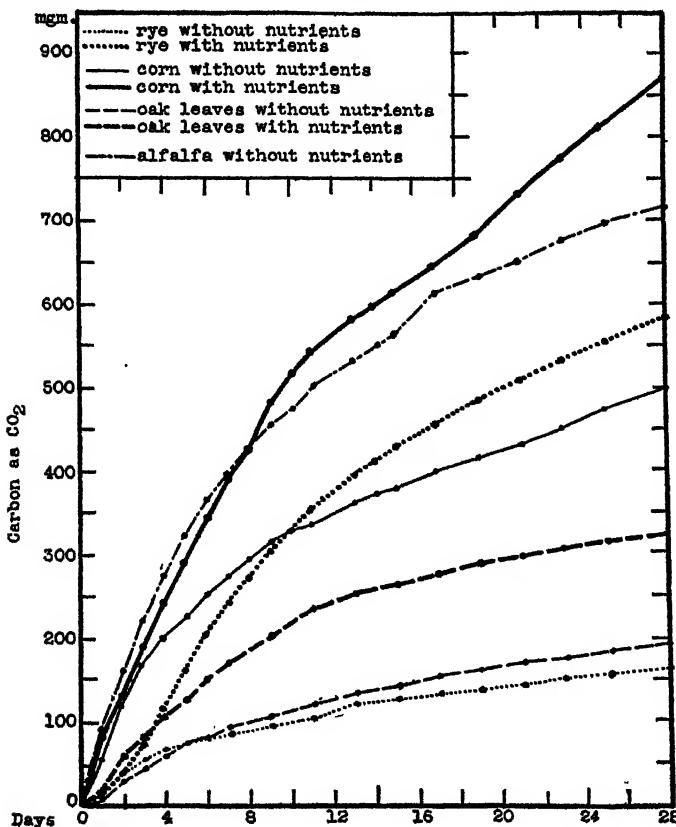


FIG. 1. COURSE OF DECOMPOSITION OF RYE STRAW, CORN STALKS, ALFALFA TOPS, AND OAK LEAVES, WITH AND WITHOUT ADDITIONAL INORGANIC NUTRIENTS, AS SHOWN BY THE EVOLUTION OF CO₂

for the wide discrepancy between the results obtained and the theoretical 100 per cent. Attention may also be called to the fact that in most analyses (the determinations of hemicellulose and cellulose based upon the sugar formed on treatment with dilute and concentrated acids), only about 95 per cent of the material is accounted for [except in the results of Kiesel (5)]. The multiplication, by 0.9, of the sugars obtained is thus apt to reduce the results for hemicellulose and cellulose by about 5 per cent.

The course of decomposition of the rye straw, corn stalks, alfalfa plant, and oak leaves as indicated by the evolution of carbon dioxide from 5 gm. of dry material, is presented in figure 1. Tables 2 to 5 give the amount of water-soluble substances, celluloses, hemicelluloses and lignins of the same materials, at the beginning and at the end of the decomposition period; also the total CO₂ liberated (recorded as mgm. of carbon) and the ammonia consumed [from the (NH₄)₂HPO₄ added] or liberated. These results are based upon the decomposition of 5 gm. of dry material at 25–26°C. for 28 days in the absence and in the presence of additional available inorganic nitrogen, phosphorus, and potash.

The addition of soluble inorganic nitrogen, phosphorus, and potash to the rye straw brought about three and one-half times as much decomposition of this material as compared with the control, or with the straw to which no inorganic nutrients were added. This comparison of the rate of decomposition should be based upon the relative amounts of CO₂ liberated. The comparison of the total residual material is not fully justified since it includes both the residual plant substance and the synthesized microbial cell-substance, and, in the presence of additional nutrients and with a considerably greater degree of decomposition, there will be much more cell substance synthesized.

The rye straw, low in nitrogen (0.24 per cent), undergoes only a very slow decomposition when no inorganic or available fertilizing elements are added. This is not due to the resistance of its constituents (celluloses, hemicelluloses, etc.) to the decomposition, but simply to the fact that the mineral nutrients necessary for the synthetic activities of the microorganisms which bring about the decomposition of the straw, are insufficient. Five grams of rye straw contain 1,696 mgm. of cellulose and 1,241 mgm. of hemicellulose, substances readily decomposable in the form in which they exist in the Gramineae. It was shown elsewhere (10) that for every 30 to 40 units of cellulose decomposed the microorganisms require 1 unit of nitrogen for the synthesis of their cell substance, when a short period of decomposition is used. To decompose 2,937 mgm. cellulose and hemicellulose, in the form of rye straw, the microorganisms would need about 70 to 95 mgm. of nitrogen, if, for the present, the decomposition of the other constituents of the straw is disregarded. The amount of rye straw used (5 gm.) contained only 12 mgm. of nitrogen. It is assumed thereby that all of this nitrogen is readily available for the activities of microorganisms. The fact that where no additional nitrogen was added only 109 mgm. of hemicellulose and 47 mgm. of cellulose were decomposed shows that not all of it is available, at least as far as the decomposition of the celluloses and hemicelluloses, which make up two-thirds of the water-insoluble organic matter of the straw, are concerned.

When inorganic mineral nutrients were added to the 5 gm. of rye straw, the decomposition was accompanied by an actual consumption of 33.9 mgm. of nitrogen by the organisms; this nitrogen was transformed from an inorganic into an organic form. This additional nitrogen enabled the microorganisms

to decompose 517 mgm. more hemicellulose and 685 mgm. more cellulose, or a total of 1,202 mgm. of cellulose and hemicellulose. The ratio between the sum of these carbohydrates decomposed and the nitrogen consumed is 35.4:1, confirming the previous conclusions concerning the ratio between the cellulose decomposition and the nitrogen requirements of the soil organisms.

Several other important conclusions can be drawn from the results of the decomposition of rye straw: When the decomposition is limited because of a lack of sufficient nutrients, or during the early stages of decomposition, the hemicellulose group, which is largely made up of pentosans in the rye straw, decomposes somewhat more rapidly than the cellulose group, a fact brought out elsewhere (10) as well as by others (4). The lignin has decomposed only to a very limited extent; the addition of available inorganic nutrients had practically no effect upon its decomposition. This emphasizes again the great resistance of the lignin to decomposition, even under aerobic conditions. It is of interest to record that the lignin in the residual material contained considerably more nitrogen than the lignin in the original straw. The nitrogen content of lignin was found to increase with an increase in the decomposition. This nitrogen, which is so resistant to treatment by acids, is derived from the cell constituents of the microorganisms, or the so-called "humin" nitrogen. In view of the fact that the lignin figures given in the tables were corrected for this nitrogen, the emphasis laid upon the resistance of the lignins to decomposition presumably need not be affected.

The results of decomposition of the corn stalks confirm and emphasize further the conclusions based on the decomposition of the rye straw. The corn stalks contained much larger amounts of water-soluble substances than did the rye straw; these substances are the first to undergo decomposition when placed under conditions favorable to the activities of microorganisms. Cold water actually extracted from the corn stalks 6 per cent of reducing sugars, based on the total plant material. The nitrogen content of the corn stalks was nearly 3 times as large as that of the rye straw, and a considerable part of it was water-soluble, or readily available.

These two factors account largely for the more rapid rate of decomposition of the corn stalks, without the addition of available nutrients, than of the rye straw. The high content of the water-soluble substances accounts for the rapid initial decomposition of the material, as shown by the rise in the CO_2 curve. When no available inorganic nitrogen was added, the curve soon flattens out so that after 10 days the corn stalks decomposed more slowly, as shown by the CO_2 curve, than did the rye straw to which inorganic nutrients were added.

In the absence of additional minerals, most of the water-soluble substances of the corn stalks were decomposed and, in addition, 395 mgm., or over 36 per cent, of the hemicelluloses, and 415 mgm., or about 29 per cent, of the celluloses. These results show again a more rapid decomposition of the hemicellulose fraction than of the cellulose fraction of a plant material in which the hemicelluloses consist largely of pentosans.

After a few days, however, when the water-soluble substances have all decomposed, the rapidity of decomposition of the corn stalks is limited by the amount of available nitrogen which is necessary for the organisms to enable them to carry on the decomposition further and to synthesize the required cell substance. It has been shown elsewhere that, unless the plant remains contain about 1.7 per cent nitrogen additional nitrogen will be required for decomposition. The 5 gm. of corn stalks contained 33 mgm. nitrogen. When additional mineral nutrients were added, almost as much more nitrogen was consumed (30.8 mgm.), or transformed from an inorganic into an organic form, as was present in the corn stalks themselves. Even then considerable cellulose and hemicellulose were left undecomposed.

The consumption of the additional 30.8 mgm. of nitrogen enabled the microörganisms to decompose 340 mgm. more hemicellulose and 468 mgm. more cellulose, a total of 808 mgm., giving a carbohydrate-nitrogen ration of a little over 26:1. The lower ratio obtained in the corn stalks as compared with that in the rye straw may either be due to the decomposition of other substances not accounted for by the sum of the celluloses and hemicelluloses (actual increased reduction in insoluble organic matter, including the synthesized substances was 3,378-2,447 or 931 mgm., which would give a ratio of 30:1 or more), or to a luxury consumption of the nitrogen by the organisms.

In the absence of additional nutrients, the corn stalks decomposed as slowly as, and no more thoroughly than the rye straw, one of the poorest and presumably most resistant groups of plant remains to which mineral nutrients have been added. With nutrients, the decomposition of the corn stalks proceeded as rapidly as that of the alfalfa plant, one of the most complete in nutrients and most readily decomposable plant materials among the plant substances commonly added to the soil.

The lignins in the corn stalks did not undergo any apparent decomposition; there was only a slight reduction in the presence of additional mineral nutrients. While the celluloses were reduced by 61.5 per cent and the hemicelluloses by 67 per cent, the lignins were reduced by only 10 per cent, in the presence of mineral nutrients, and by a mere trace in their absence.

The initial rate of decomposition of the alfalfa plant proceeded more rapidly than that of any of the other organic substances, because of the highest content of cold-water-soluble substances. The total decomposition of the alfalfa proceeded further than that of any of the other plant substances, without the addition of mineral nutrients, but not so far as that of the corn stalks to which inorganic nutrients were added. Just as the curve of evolution of CO₂ for the rye straw with nutrients rose after 10 days above the curve for the corn stalks without nutrients, so the curve of evolution of CO₂ of the corn stalks with nutrients rose after 8 days above the corresponding curve for alfalfa.

There was no lack of sufficient nitrogen in the alfalfa plant, since 24.2 mgm. of nitrogen was liberated as ammonia within 28 days. This is because the nitrogen content of the alfalfa was above 1.7 per cent, and, as shown elsewhere

(10), one would then expect that the excess of nitrogen should become readily liberated in an available form. In the case of the alfalfa plant as well, there was a relatively more rapid decomposition of the hemicelluloses than of the celluloses. A large part of the CO₂ has come, however, from the decomposition of the water-soluble substances and of the proteins.

The lignins in the alfalfa were not diminished as a result of decomposition; there was an actual increase in the lignin content. This may be due either to the synthesizing activities of the microorganisms, which result in the formation of so-called "humus" complexes that behave like the lignins, or to the fact that the alcohol-soluble constituents have not been removed from the residual plant material, but have been accounted for in the initial material. This non-removal of the alcohol-soluble fraction (table 1) would tend to give a somewhat higher lignin figure than would otherwise be the case, especially in alfalfa which contained a large alcohol-soluble fraction, since a part of the alcohol-soluble material would come down with the lignin.

The decomposition of the oak leaves shows that the amount of total nitrogen present in the plant material is not the only factor which controls the rapidity of decomposition. These leaves contained three times as much nitrogen as the rye straw, but the rapidity of decomposition, in the absence of additional inorganic nutrients, was about the same. The high content of waxy substances, on the one hand, and of lignins, on the other, delayed the decomposition of the oak leaves. This is further emphasized by the fact that, when inorganic nutrients were added, the decomposition of the rye straw was favored to a much greater extent than was that of the oak leaves. In the decomposition of rye straw, the lack of nutrients is the most important limiting factor, whereas in that of the leaves, the presence of certain substances interferes with the speed of decomposition.

The water-soluble substances in the oak leaves were also the first to undergo decomposition. The hemicelluloses were decomposed more rapidly than the celluloses and the lignins were resistant to decomposition. The fact that there was a greater reduction in the sum of the cellulose and hemicellulose than of the total insoluble organic matter points either to the synthesis of cell substance by microorganisms or to their transformation into other insoluble substances. The fact that the decomposition of the oak leaves allows considerable synthesis of the cell substance is brought out in the relatively narrow ratio between the sum of the cellulose and hemicellulose decomposed and the nitrogen consumed when inorganic nutrients were added. It is also possible that the high nitrogen consumption may be due to the decomposition of some of the other constituents of the leaves besides the celluloses and hemicelluloses.

It has been shown elsewhere (10) that the removal of certain groups of the plant constituents may influence favorably the processes of decomposition. In the case of barley straw, the removal of the ether-soluble materials hastened somewhat the decomposition of the residual material; whereas the removal of both the ether- and the alcohol-soluble substances retarded somewhat the

decomposition, as shown by the evolution of carbon dioxide. This is because while ether removes the fats and waxes which may form a coating over the plant material and thus prevent somewhat rapid decomposition, alcohol also removes the sugars and some of the amino acids, substances which are most readily decomposable.

Mature pine needles and sphagnum moss were selected for this study. An analysis of these two materials is given in table 1. Several portions of each

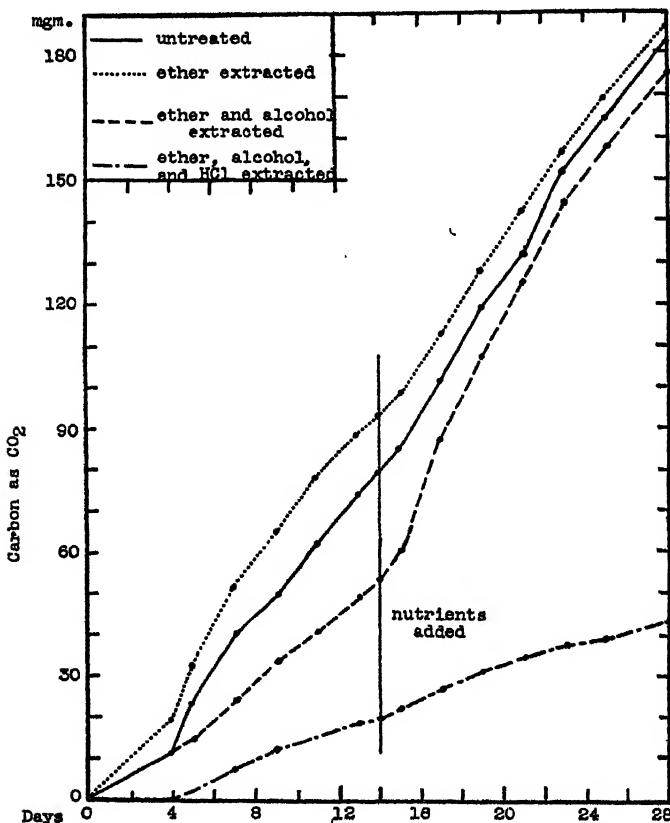


FIG. 2. COURSE OF DECOMPOSITION OF PINE NEEDLES FROM WHICH DIFFERENT FRACTIONS HAVE BEEN REMOVED

of the air-dry materials were taken in amounts equivalent to 5 gm. of dry matter. Some were left untreated; some were treated with ether for 24 hours in soxhlet extractors; some were treated with ether and then with boiling 95 per cent alcohol for 1 hour; some were treated with ether, alcohol, then with 2 per cent hydrochloric acid solution for 1 hour, under a reflux condenser. The residues, after all the treatments, were placed in flasks, water was added to adjust the moisture to 200 per cent and the materials were inoculated with a

suspension of fresh soil. No detailed analyses were made at the end of the decomposition period. The CO_2 given off and the amount of ammonia nitrogen liberated and absorbed were the only two indices used for measuring the rapidity and the amount of decomposition, which are given in table 6 and in figures 2 and 3.

The pine needles decomposed even more slowly than the oak leaves; the removal of the ether-soluble fraction hastened somewhat the rapidity of decom-

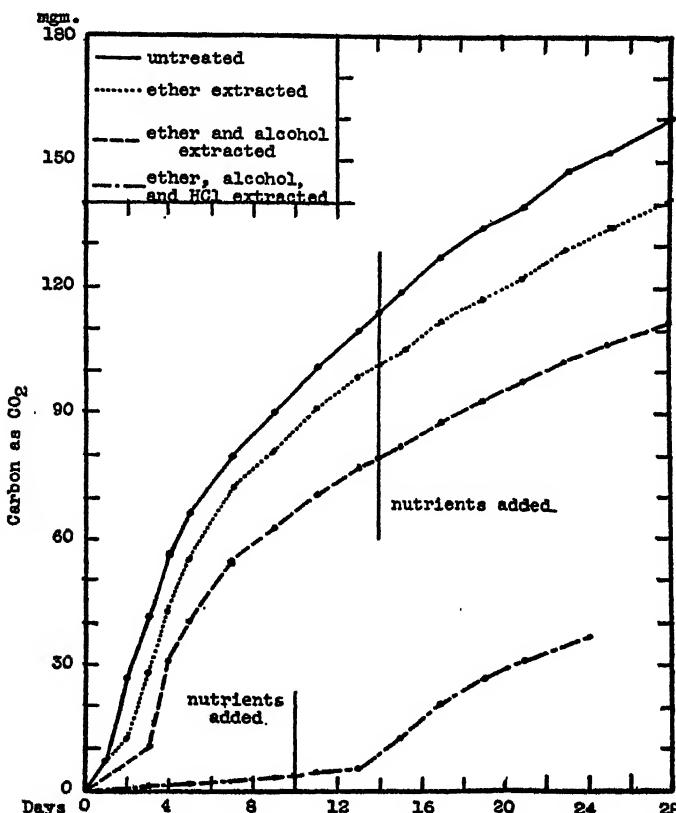


FIG. 3. COURSE OF DECOMPOSITION OF SPHAGNUM FROM WHICH DIFFERENT FRACTIONS HAVE BEEN REMOVED

position, while the removal of the ether- and alcohol-soluble fraction delayed decomposition. The acid-treated material (the acid-soluble substances being removed) decomposed only very slowly, probably because of the removal of the easily decomposable substances, especially the proteins and pentosans. After the materials were decomposed for 14 days, additional inorganic nutrients were added, as outlined above. This resulted in an immediate rise in the rapidity of decomposition in all the treated materials. The decomposition,

as measured by the amount of CO_2 liberated, was accompanied by an absorption of nitrogen and its transformation from an inorganic into an organic form. These results substantiate the previous investigations with rye straw.

The decomposition of the sphagnum moss, which has been treated in a manner similar to the pine needles, shows an entirely different set of relationships:

1. Ether treatment removed some easily decomposable substances and hence reduced the rate of decomposition. Treatment with ether and with alcohol served to retard decomposition even further, because the alcohol removed an even larger proportion of readily

TABLE 6
Influence of treatment upon the decomposition of sphagnum plants and needles of Pinus strobus
(On the basis of original 5 gm. of dry material)

TREATMENT	SPHAGNUM PLANT		NEEDLES OF PINUS STROBIS	
	CO_2 given off	Ammonia liberated (+) or absorbed (-)	CO_2 given off	Ammonia liberated (+) or absorbed (-)
Untreated.....	mgm. C	mgm. N	mgm. C	mgm. N
Ether-soluble portion removed.....	160.4	+3.2	183.6	-9.2
Ether- and alcohol-soluble portions removed.....	141.3	+4.0	186.8	-9.4
Ether-, alcohol-, and dilute-acid- (2 per cent HCl) soluble portions removed.....	112.4	+0.2	175.0
	36.6	-5.6	42.7	-4.0..

TABLE 7
Decomposition of different parts of Leucobryum, in the presence and absence of nutrients
(On the basis of original 5 gm. of dry material)

PART OF PLANT USED	CO_2 given off	NH ₃ LIBERATED (+) OR ABSORBED (-)	
		mgm. C	mgm. N
Upper growing portion of plant.....	147.9	+8.2	
Lower dead portion, no nutrients.....	107.7	+1.0	
Lower dead portion + nutrients.....	125.2	-10.6?	

decomposable substances (probably nitrogen compounds, as shown by the liberation of ammonia) from the alcohol-treated than from the untreated and ether-treated materials.

2. Although the sphagnum moss is relatively poor in nitrogen, the addition of available nitrogen and phosphorus did not stimulate further decomposition. The addition of these inorganic nutrients, which had such a marked effect in stimulating the decomposition of rye straw and corn stalks, was without any effect upon the decomposition of the sphagnum moss, a plant material not very rich in nitrogen and phosphorus. The addition of inorganic nutrients had a marked effect, however, upon the decomposition of the moss treated with ether, alcohol, and acid, the latter treatment having brought about the hydrolysis and removal of the available nitrogen complexes of the plant.

3. The decomposition of the untreated or ether-treated sphagnum moss was accompanied by a rapid liberation of some of the nitrogen as ammonia. This is no doubt due to two factors: (a) the nitrogen complexes of the sphagnum are readily decomposable; (b) the non-

nitrogen complexes are slowly decomposable, hence the microorganisms active in the decomposition are not supplied with sufficient energy to enable them to reassimilate the nitrogen liberated and to transform it into microbial cell substance. This mechanism explains the ability of the sphagnum plant to grow in bogs which are only very poorly supplied with nitrogen, since the dead plant rapidly gives off a part of its nitrogen, which can then be readily used again by the growing plant. This phenomenon will be brought out in detail in another paper.

To compare the decomposition of the living and the dead portions of a moss, the *Leucobryum* plant was selected. The upper, green, living portions were

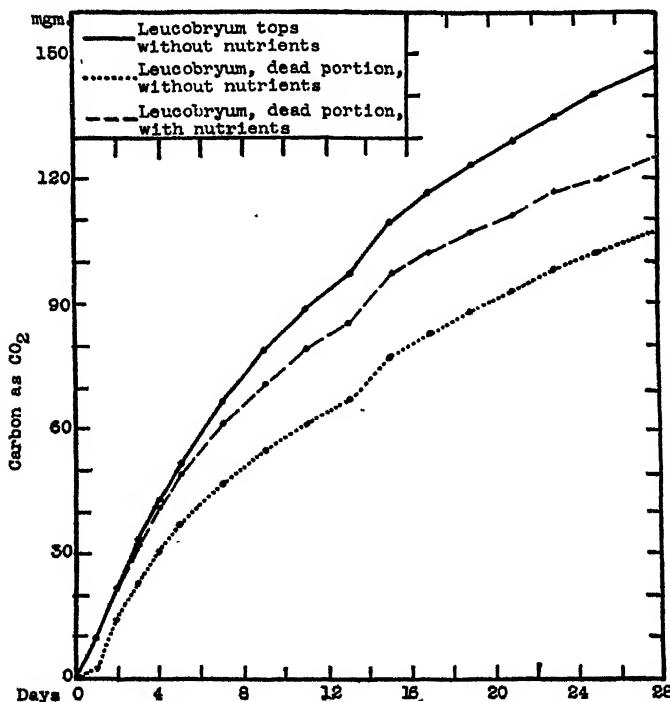


FIG. 4. COURSE OF DECOMPOSITION OF THE LIVING AND DEAD PORTIONS OF LEUCOBRYUM MOSS, WITH AND WITHOUT NUTRIENTS

separated from the lower, brown, dead portions. The dead portion is considerably lower in nitrogen and higher in lignin than the living portion, indicating that considerable decomposition has already taken place.

A study of the decomposition of the two portions shows (table 7) that the living is much more rapidly decomposed than the dead (fig. 4). This decomposition was accompanied by the liberation of considerable nitrogen as ammonia from the living portion and only a trace from the dead portion. There was actually some consumption of nitrogen when inorganic nutrients were added to the dead plants.

SUMMARY

The results presented in this paper show conclusively that the rapidity of decomposition of plant remains and the nature of decomposition depend upon at least several factors:

1. *Nature of plant.* Different plants will vary in composition, which will markedly influence the decomposition processes. Some plant constituents may decompose more readily than others; some substances may even retard the decomposition of other substances.

2. *Age of plant.* The younger the plant and the less mature it is, the more rapid will be the rate of its decomposition. The decrease in the relative nitrogen and ash content and of the total water-soluble substances and the increase of the cellulose and lignin content, with an increase in maturity of the plant will account for its slower decomposition.

3. *Presence of available inorganic nutrients.* In most plants, especially when they are mature, there is a lack of balance between the available carbohydrates and the available nitrogen and minerals required by the microorganisms which bring about the decomposition of the plant. In those cases, the presence of additional inorganic nutrients will greatly hasten the decomposition processes.

4. A number of other factors, such as nature of microflora and microfauna active in the decomposition, proper aeration, and soil reaction, modify the rapidity and nature of decomposition of the plant material.

5. These factors influence the rate of evolution of CO₂, the amount of "humus" or soil organic matter resistant to decomposition that is formed, and the rapidity of liberation of nitrogen and of mineral plant constituents.

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POTATO PLANTS GROWN IN MINERAL NUTRIENT MEDIA

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A few years ago the writer (3) carried out a series of sand culture experiments dealing with the mineral nutrient requirement of the potato plant. The method employed followed rather closely the general plan (6) of the committee on salt requirements of representative agricultural plants, National Research Council. In a recent article Gregory (1) emphasized the importance of estimating the effect of various single ions on plant yield when these ions are present in mixtures of salts and he has made some very interesting analyses of the writer's data. As mentioned by Gregory and as realized by the writer, a just criticism of the work was made because the experiments were performed over several years and at different seasons of these years. No attempt at climatic control was made. The purpose of the present paper is to point out another criticism of the original work which, like that concerning the climatic factors, probably does not invalidate the *relative* yield values found for plants grown in different culture media, but without a doubt it does greatly influence the *actual* yields.

In the original paper (3) the statement was made that "The actual amount of growth was greater for plants treated with type I solutions than for the plants of the other five types." The reason for such marked differences was at that time and until recently an unsolved problem. Later the best cultures of each type were grown under the same environmental conditions, and data from four such experiments were presented in another paper (4). In spite of the care used and the repetition of the experiments none of the plants ever grew as well as those of the first two series of type I, which were the first to be studied.

A possible explanation of this unsolved problem was suggested by D. R. Hoagland of the University of California. This suggestion grew out of observations on tomato plants grown in boron-deficient solutions (5). The growing point of the stems of these plants soon died, thus preventing further stem elongation. Similar symptoms but less severe had been noted in the later sand culture experiments with potatoes. If a lack of boron were the true explanation then the more vigorous growth obtained in the first two series could be attributed to a sufficient quantity of boron being dissolved from the glaze of the new earthenware jars and then being used by the plants of these first two experiments. In later experiments the amount of soluble boron removed from the glaze was not sufficient for the plant's requirements.

This theory was put to a test by repeating a series of experiments in which solution R_8S_4 of type I was used. Six culture jars were used each containing three plants. To three of these cultures boron (0.55 p.p.m.) as boric acid was added. The same glazed jars that had been used in the previous experiments were again used, as well as the same general methods. The potato sprouts were set out in the sand cultures on March 12 and harvested May 7, 1928. The data from this single simple experiment are presented in tables 1 and 2, where the differences in growth between the boron deficient plants

TABLE 1
Average weekly height and total weekly transpiration per plant

WEEK ENDING	AVERAGE HEIGHT		AVERAGE TOTAL WEEKLY TRANSPIRATION	
	A Boron deficient	B Boron added	A Boron deficient	B Boron added
1928	cm.	cm.	cc.	cc.
March 19.....	33	30	13	14
March 22.....	41	40	52	57
April 2.....	57	59	69	91
April 9.....
April 16.....	75	86	232*	369*
April 23.....	74	93	112	245
April 30.....	74	96	108	274
May 7.....	76	101	46	271

* Average for 2 weeks.

TABLE 2
Average dry weight of tops and roots and average green weight and number of tubers per plant

	DRY WEIGHTS			TUBERS	
	Tops	Roots	Total	Green weight	Number
A. Boron deficient.....	gm.	gm.	gm.	gm.	
B. Boron added.....	1.4	0.7	2.1	9.2	1.3
	2.4	0.8	3.2	21.1	1.8

and those receiving boron are clearly seen. The appearance of two representative cultures photographed at date of harvest is illustrated in plate 1, figure 1.

This experiment, though not so extensive as those previously reported, clearly shows the importance of boron to the growth of the potato plant in pure sand cultures. Although the climatic factor, of necessity, was neglected in these studies and its importance realized, this other factor of equal and perhaps greater importance was overlooked. As methods and technic become more and more refined still other factors will limit deductions drawn from

earlier experiments, perhaps not altering their qualitative relations, but certainly making them quantitatively doubtful.

One other observation regarding the growth of potato plants in nutrient media is of interest and may prove important in studying the relation of ions to the growth of this plant. Numerous difficulties have been encountered when potatoes are grown in water cultures. One of these seems to be related to the question of aeration. Skinner (8), Johnston (2), Newton (7), and others have reported methods used in dealing with the problem, but nothing very satisfactory has been found.

Because of the ease with which tomato plants grow in water cultures a set of 20 potato seedlings was set in paraffined cork stoppers and fitted into 2-quart jars in a manner similar to water culture methods employed where wheat, buckwheat, and barley are used.¹ One half the cultures contained solutions deficient in boron. To the other half, boron (0.55 p.p.m.) as boric acid was added. Very good vine growth was obtained in cultures containing boron. Even though no method was used for aerating the roots, root growth was excellent. The plants grown in boron-deficient solutions soon showed very interesting characteristics. The tip of the terminal shoot died and soon dried up, the leaves became thick and rolled in a manner characteristic of potato leaf-roll disease. Microscopic examination of leaf tissue showed the presence of starch in abundance, and darkened dead areas were evident in the region of the phloem in cross sections of the stem and petiole. Figure 2 of plate 1 brings out the marked diseased condition of the boron-deficient plant when compared to the normal one.

This method of growing potato plants in water cultures is extremely simple and promises much as a means of ascertaining the effects of various chemicals on growth under highly controlled conditions. Its great disadvantage is the use of plants grown from seeds which, in this case, are extremely variable. In this particular experiment the effect of boron is clear, since all ten plants grown in the boron-deficient solutions showed the same severe and similar symptoms while the plants grown in solutions containing boron showed none of these symptoms. Plants in each group did, however, differ somewhat in size and character of growth, which was to be expected.

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¹ These seedlings were grown in a bed of soil from potato seeds obtained from L. L. Olds Seed Company of Madison, Wisconsin.

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PLATE 1

FIG. 1. Potato plants grown in sand cultures treated with boron-deficient solution (left) and with a similar solution to which boron had been added (right).

FIG. 2. Potato seedlings grown in water cultures, one (left) containing a boron-deficient solution, the other (right) a similar solution to which boron had been added.



FIG. 1



FIG. 2

THE NITROGEN-FIXING MICROORGANISMS OF AN ARID SOIL¹

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The dry-farm soils of Utah are low in nitrogen, and it is the exception to find a farm on which a legume is systematically grown or one which receives nitrogen-carrying manures. Yet many of these soils have produced good crops for years. In fact, analysis of such soils after 50 years of cropping often shows more nitrogen in the surface foot of the cropped soil than in the adjoining virgin soil. Most of the soils so far tested actively fix nitrogen when incubated with an optimum moisture content at a temperature of 28°C. This is true of some soils even when incubated without the addition of a carbohydrate (2).

The soil of the Nephi Experimental Farm is especially interesting, for it is highly productive, does not contain the azotobacter, and actively fixes nitrogen. In some vegetation house experiments, extending over several years, gains of 35 pounds per acre-foot have been repeatedly obtained, and where appropriate sources of energy in the form of straw and plant residues have been added the gain has been several times this amount (4). The soil contains in the surface acre-foot 4108 pounds of nitrogen, 86,300 pounds of potassium, 7305 pounds of phosphorus, 97,200 pounds of carbon, 41,830 pounds of organic carbon, 69,260 pounds of magnesium carbonate, and 138,800 pounds of calcium carbonate. The fact that this soil fixes nitrogen actively and yet does not contain the azotobacter raised the following questions: What organisms are fixing nitrogen in this soil? Are there any conditions in this soil which render it inimical to the growth of the azotobacter? This paper deals with the first question.

NUMBER OF ORGANISMS IN SOIL

The air-dry soil was pulverized and counts made by the plate method. Three different media were used—a beef extract agar, a synthetic agar, and an Ashby mannite agar. The average for 24 determinations was as follows:

Beef extract agar.....	19,526,000
Ashby mannite agar.....	19,080,000
Synthetic agar.....	12,725,000

¹ Contribution from Department of Bacteriology and Chemistry, Utah Agricultural Experiment Station, Logan, Utah. Approved for publication by Director, May 8, 1928.

² Associate bacteriologist and assistant in department, respectively. The authors acknowledge herewith the helpful suggestions of Dr. J. E. Greaves, which have been ever at their disposal.

Practically the same number of colonies developed on the Ashby mannite agar, which was free from combined nitrogen, as developed upon the beef extract agar. The number developing on the synthetic agar was only 66 per cent of those developing upon the beef extract agar.

The various colonies which developed upon the Ashby mannite agar were selected and the respective organisms were obtained in pure cultures. These were studied morphologically and physiologically, according to the methods of the Society of American Bacteriologists. The organisms obtained were as follows:

Actinomyces albocinereus

Branched filaments with open and closed spirals. Conidia not observed. Non-motile. Gram-positive.

Gelatin colonies: Light gray, irregular, crateriform, filamentous.

Gelatin stab: Liquefaction, crateriform, medium browned.

Agar colonies: Very light gray, filamentous, concentrically-ringed, raised.

Agar slant: Light gray, scanty to moderate growth, beaded, raised, dull, rugose.

Broth: Pellicle, turbid, abundant flocculent sediment.

Litmus milk: Peptonized.

Potato: Steel gray, medium blackened.

Starch: Hydrolyzed.

Acid formed in sucrose.

Indol is formed.

Nitrates not reduced.

Nitrogen fixation: 1.65 mgm. in 100 gm. of soil.

Aerobic.

Optimum temperature: 35°C.

Habitat: Soil.

Actinomyces cinereus

Straight and slightly curved filaments, with few branches. Conidia oval. Non-motile. Gram-positive.

Gelatin colonies: Small irregular, raised, undulate.

Gelatin stab: Liquefaction, crateriform, browned.

Agar colonies: Whitish-gray, filamentous, rough, raised.

Agar slant: Whitish-gray, moderate, beaded, dull, rugose, membranous, medium slightly browned.

Broth: Moderate turbidity with abundant flocculent sediment.

Litmus milk: Unchanged.

Potato: No growth.

Starch: Hydrolyzed.

Acid formed in dextrose, lactose, and sucrose.

Indol is formed.

Nitrates not reduced.

Nitrogen fixation: 2.7 mgm. in 100 gm. of soil.

Aerobic.

Optimum temperature: 35°C.

Habitat: Soil.

Actinomyces exfoliatus, n. v.

Wavy filaments with tendency to form spirals. Conidia spherical to oval, 1.0 to 1.5 μ . Non-motile. Gram-positive.

Gelatin colonies: Irregular, raised, lobate, medium yellowish-brown.

Gelatin stab: Liquefaction, crateriform.

Agar colonies: Growth rapid, circular, rough, raised, filamentous.

Agar slant: Moderate, beaded, raised, dull, contoured, membranous, browned.

Broth: Small brownish-gray colonies throughout medium, slightly turbid with abundant compact sediment.

Litmus milk: Peptonized.

Potato: Light brown.

Starch: Hydrolyzed.

Acid formed in dextrose.

Indol is formed.

Nitrates reduced to nitrites.

Nitrogen fixation: 1.15 mgm. in 100 gm. of soil.

Aerobic.

Optimum temperature: 37°C.

Habitat: Soil.

Actinomyces fradii, n. v.

Straight, branching filaments. No spirals. Conidia oval, 0.5 to 1.0 μ . Non-motile, gram-positive.

Gelatin colonies: Brownish, filamentous, slightly raised, lobate.

Gelatin stab: Liquefied, browned.

Agar colonies: Transparent to yellowish, circular, slow growth, rough, raised, filamentous.

Agar slant: Transparent to yellowish, scanty, beaded, flat to slightly raised, dull, slightly rugose, butyrous.

Broth: Slightly turbid, with abundant flocculent sediment.

Litmus milk: Peptonized.

Potato: Restricted, orange-colored.

Starch: Hydrolyzed.

Acid is formed in dextrose, lactose, sucrose.

Indol not formed.

Nitrates not reduced.

Nitrogen fixation: 1.3 mgm. in 100 gm. of soil.

Aerobic.

Optimum temperature: 25°C. to 30°C.

Habitat: Soil.

Actinomyces filatosus

Long filaments, straight with little tendency to form spirals. Few oval conidia formed. Non-motile. Gram-positive.

Gelatin colonies: Small, yellowish-brown, raised, filamentous.

Gelatin stab: Liquefied, browned.

Agar colonies: Grayish, circular, raised, filamentous.

Agar slant: Grayish, moderate growth, beaded, raised, dull contoured, membranous, medium slightly browned.

Broth: Turbid with abundant flaky sediment.

Litmus milk: Peptonized.

Potato: Grayish growth, medium purplish-brown.

Starch: Hydrolyzed.

Acid formed in sucrose.

Indol is formed.

Nitrates show very slight reduction to nitrites.

Nitrogen fixation: 0.6 mgm. in 100 gm. of soil.

Aerobic.

Optimum temperature: 35°C.

Habitat: Soil.

Actinomyces negrocinerous

Straight and curved filaments with short branches. Closed spirals, conidia oval shaped.

Non-motile. Gram-negative.

Gelatin colonies: Grayish-brown circular, raised, filamentous.

Gelatin stab: Liquefaction, infundibuliform, yellowish-brown.

Agar colonies: Grayish-brown, circular, rough, raised, filamentous.

Agar slant: Moderate growth, beaded, raised, dull, rugose, brittle, medium browned.

Broth: Slightly turbid with abundant flocculent sediment.

Litmus milk: Peptonized.

Potato: Purplish gray.

Starch: Hydrolyzed.

Acid formed in lactose.

Indol is formed.

Nitrates show very slight reduction to nitrites.

Nitrogen fixation: 4.1 mgm. in 100 gm. of soil.

Aerobic.

Optimum temperature: 35°C.

Habitat: Soil.

Actinomyces negroflavus

Straight and curved, branched filaments, with few spirals and few rod shaped conidia.

Non-motile. Gram-negative.

Gelatin colonies: Dirty yellow, circular, convex, undulate.

Gelatin stab: Liquefaction, crateriform, medium yellowish-brown.

Agar colonies: Dirty cream, circular, rough, convex, filamentous.

Agar slant: Dirty cream, moderate growth, beaded, raised, dull, rugose, membranous.

Broth: Slightly turbid with abundant flocculent sediment.

Litmus milk: Slightly acid, insufficient for curdling.

Potato: No growth.

Starch: Hydrolyzed.

Acid formed in dextrose.

Indol not formed.

Nitrates not reduced.

Nitrogen fixation: None in soil.

Aerobic.

Optimum temperature: 35°C.

Habitat: Soil.

Actinomyces roseus purpureus

Straight and slightly wavy filaments, with spirals. Branched, conidia oval to spherical.

Non-motile. Gram-positive.

Gelatin colonies: Small, circular, slightly raised, filamentous.

Gelatin stab: Liquefied.

Agar colonies: Reddish-purple, irregular, rough, convex, filamentous.

Agar slant: Reddish-purple, moderate growth, beaded, raised, dull, rugose, butyrous, medium reddish-brown.

Broth: Turbid, with abundant flaky sediment.

Litmus milk: Unchanged.

Potato: Purplish-brown, abundant.

Starch: Hydrolyzed.

No acid or gas formed in dextrose, lactose, sucrose.

Indol not formed.

Nitrates not reduced.

Nitrogen fixation: 5.85 mgm. in 100 gm. of soil.

Aerobic.

Optimum temperature: 35°C.

Habitat: Soil.

Actinomyces sphaerulosus

Branching filaments, with spirals. Conidia oval to elongate. Non-motile. Gram-positive.

Gelatin colonies: Small, brownish.

Gelatin stab: Liquefaction rapid, medium browned.

Agar colonies: Circular, brownish-white, rough, convex, filamentous.

Agar slant: Brownish-white, moderate, beaded, raised, dull contoured, membranous.

Broth: Slightly turbid with scanty sediment.

Litmus milk: Unchanged.

Potato: Dull dry gray.

Starch: Hydrolyzed.

No acid or gas formed in dextrose, lactose, sucrose.

Indol not formed.

Nitrates show very slight reduction to nitrites.

Nitrogen fixation: 2.7 mgm. in 100 gm. of soil.

Aerobic.

Optimum temperature: 35°C.

Habitat: Soil.

Actinomyces undulatus

Thick, wavy, branched filaments. No spirals. Conidia rod or oval shape. Non-motile. Gram-negative.

Gelatin colonies: Steel-gray, with whitish center, circular, raised filamentous.

Gelatin stab: Liquefaction, crateriform slightly browned.

Agar colonies: Steel-gray, rapid growth, rough, raised, filamentous.

Agar slant: Steel-gray, abundant, beaded, raised, dull rugose, membranous to brittle.

Broth: Slight turbidity with abundant flocculent sediment.

Litmus milk: Peptonized.

Potato: No growth.

Starch: Hydrolyzed.

No acid or gas formed in dextrose, lactose, sucrose.

Indol not formed.

Nitrates not reduced.

Nitrogen fixation: 2.7 mgm. in 100 gm. of soil.

Aerobic.

Optimum temperature: 35°C.

Habitat: Soil.

Bacillus annulofaciens

Rods: 1.0 to 1.5 by 3.0 to 8.0 μ with rounded ends, occurring singly and in chains. Non-motile. Spores excentric to terminal, 1.0 to 1.5 μ . Gram-positive.

Gelatin colonies: Yellowish-brown, growth rapid, irregular, flat, lobate, liquefaction saucer-like.

Gelatin stab: Liquefaction napiform, rapid.

Agar colonies: Cream-gray, growth rapid, irregular, rough, slightly raised, undulate.

Agar slant: Cream-gray, growth abundant, spreading, slightly raised, dull, rugose, butyrous.

Broth: Ring, moderate turbidity with abundant flocculent sediment.

Litmus milk: Peptonized.

Potato: No growth.

Starch: Hydrolyzed.

No acid or gas formed in dextrose, lactose, sucrose.

Indol not formed.

Nitrates reduced to nitrites.

Nitrogen fixation: 1.3 mgm. in 100 gm. of soil

Aerobic.

Optimum temperature: 30°C.

Habitat: Soil.

Bacillus aridii

Rods: 1.0 by 2.0 to 6.0 μ , occurring singly and in short chains. Non-motile. Spores central, 1.0 to 1.2 μ . Gram-positive.

Gelatin colonies: Transparent, rapid growth, irregular, flat, lobate, liquefaction spreading.

Gelatin stab: Liquefaction crateriform, browned.

Agar colonies: Whitish cream, growth rapid, circular, smooth, raised, entire.

Agar slant: Whitish cream, growth moderate, beaded, raised, glistening, rugose, butyrous.

Broth: Turbid, with scanty flocculent sediment.

Litmus milk: Peptonized.

Potato: No growth.

Starch: Hydrolyzed.

Acid formed in lactose and sucrose.

Indol not formed.

Nitrates not reduced.

Nitrogen fixation: 0.25 mgm. in 100 gm. of soil.

Aerobic.

Optimum temperature: 30°C.

Habitat: Soil.

Bacillus viridis pallens

Rods: 1.0 by 2.0 to 4.0 μ , with tapering ends, occurring singly and in chains. Non-motile, spores polar, 1.0 by 2.0 μ . Gram-negative.

Gelatin colonies: Whitish, punctiform, flat, entire.

Gelatin stab: Liquefaction infundibuliform.

Agar colonies: Gray, small, circular, rough, convex, entire.

Agar slant: Gray, scanty growth, beaded, slightly raised, dull, rugose, opaque, butyrous.

Broth: Turbid with abundant flocculent sediment.

Litmus milk: Peptonized.

Potato: Greenish-gray.

Starch: Hydrolyzed.

Acid formed in dextrose, lactose, sucrose.

Indol not formed.

Nitrates not reduced.

Nitrogen fixation: 3.4 mgm. in 100 gm. of soil.

Aerobic.

Optimum temperature: 30°C.

Habitat: Soil.

Bacillus indoliciens

Rods: 0.8 to 1.0 by 2.0 to 3.0 μ , with tapering ends, occurring singly and in chains. Motile, spores central, spherical, 1.0 to 1.5 μ . Gram-positive.

Gelatin colonies: Grayish, slow growth, circular, raised, entire.

Gelatin stab: Liquefaction stratiform.

Agar colonies: Light gray, large, circular, slightly raised, entire.

Agar slant: Light gray, moderate growth, spreading, flat, glistening, smooth, translucent, viscid.

Broth: Slightly turbid with grayish pellicle and scanty flaky sediment.

Litmus milk: Peptonized.

Potato: Grayish.

Starch: Hydrolyzed.

No acid or gas formed in dextrose, lactose, sucrose.

Indol is formed.

Nitrates not reduced.

Nitrogen fixation: 1.15 mgm. in 100 gm. of soil.

Aerobic.

Optimum temperature: 25°C. to 30°C.

Habitat: Soil.

Bacillus levanensis

Rods: 1.0 by 2.0 to 4.0 μ with rounded ends, occurring singly and in short chains. Motile, spores, central 1.5 by 2.0 μ . Gram-positive.

Gelatin colonies: Light brown, large, irregular, undulate, liquefaction saucer-like.

Gelatin stab: Liquefaction infundibuliform, rapid, medium browned.

Agar colonies: Light brown to black, large, irregular, rough, slightly raised, lobate.

Agar slant: Light brown to black, abundant, spreading, slightly raised, dull, rugose, membranous, medium browned.

Broth: Membranous, turbid, with abundant flaky sediment.

Litmus milk: Peptonized.

Potato: Dark brown to black, abundant, medium blackened.

Starch: Hydrolyzed.

Acid formed in dextrose, lactose, and sucrose.

Indol not formed.

Nitrates reduced to nitrites.

Nitrogen fixation: 4.8 mgm. in 100 gm. of soil.

Aerobic.

Optimum temperature: 30°C.

Habitat: Soil.

Bacillus multumerescens

Rods: 0.8 to 1.0 by 3.0 to 5.0 μ , with rounded ends, occurring singly and in chains. Non-motile, spores polar, 0.8 by 2.0 μ . Gram-positive.

Gelatin colonies: Grayish, circular, slightly raised, entire, liquefaction, saucer.

Gelatin stab: Liquefaction saccate.

Agar colonies: Light gray, circular, concentrically ringed, flat, entire.

Agar slant: Light gray, abundant, filiform, slightly raised, glistening, slightly contoured, opalescent, viscid.

Broth: Turbid, with grayish pellicle and abundant sediment.

Litmus milk: Peptonized.

Potato: Grayish-cream, abundant.

Starch: Hydrolyzed.

No acid or gas formed in dextrose, lactose, sucrose.

Indol not formed.

Nitrates not reduced.

Nitrogen fixation: 1.3 mgm. in 100 gm. of soil.

Aerobic.

Optimum temperature: 30°C.

Habitat: Soil.

Bacillus nephii

Rods: 1.0 to 1.5 by 3.0 to 6.0 μ , occurring singly and in chains. Motile by means of peritrichous flagella. Spores central or excentric, thin walls, 1.5 to 2.0 by 2.0 to 2.5 μ . Gram-positive.

Gelatin colonies: Whitish-gray, slow, punctiform.

Gelatin stab: Liquefaction slow crateriform.

Agar colonies: Dirty gray, rapid growth, circular, smooth, slightly raised, entire.

Agar slant: Dirty gray, moderate growth, filiform or slightly beaded, raised, glistening, smooth, translucent, viscid.

Broth: Turbid with abundant flaky sediment.

Litmus milk: Slightly acid, insufficient for curdling.

Potato: No growth.

Starch: Not hydrolyzed.

Acid formed in dextrose and sucrose. Acid and gas formed in lactose.

Indol not formed.

Nitrates reduced to nitrites.

Nitrogen fixation: 1.3 mgm. in 100 gm. of soil.

Aerobic.

Optimum temperature: 30°C.

Habitat: Soil.

Bacillus subfuscus

Rods: 1.0 to 1.5 by 3.0 to 5.0 μ , occurring singly and in chains. Non-motile. Spores excentric to terminal 1.5 to 2.0 by 2.0 to 2.5 μ . Gram-positive.

Gelatin colonies: Light brown, rapid growth, irregular, raised, filamentous, saucer liquefaction.

Gelatin stab: Liquefaction crateriform, rapid, browned.

Agar colonies: Dirty cream, large, circular, slightly ringed, flat, entire.

Agar slant: Dirty cream, abundant, spreading, flat, glistening, smooth, opaque, butyrous.

Broth: Clear with pellicle and scanty sediment.

Litmus milk: Unchanged.

Potato: No growth.

Starch: Hydrolyzed.

Acid formed in dextrose, lactose, sucrose.

Indol not formed.

Nitrates reduced to nitrites.

Nitrogen fixation: 2.7 mgm. in 100 gm. of soil.

Aerobic.

Optimum temperature: 30°C.

Habitat: Soil.

Micrococcus cinereus

Spheres: 0.5 to 1.0 μ , occurring singly, in pairs, and in clumps. Gram-positive.

Gelatin colonies: No growth.

Gelatin stab: No growth.

Agar colonies: Grayish cream, circular, smooth, raised, entire.

Agar slant: Grayish cream, filiform, raised, glistening, smooth, viscid.

Broth: Turbid with scanty flaky sediment.

Litmus milk: Unchanged.

Potato: Cream becoming grayish.

Starch: Hydrolyzed.

Acid in dextrose, lactose, and sucrose.

Indol not formed.

Nitrates not reduced.

Nitrogen fixation: 5.15 mgm. in 100 gm. of soil.

Aerobic.

Optimum temperature: 30°C.

Habitat: Soil.

Micrococcus conglomeratus, n. v.

Spheres: 1.0 to 1.5 μ , occurring singly, in pairs, and in clumps. Gram-positive.

Gelatin colonies: Yellow, small circular.

Gelatin stab: Slow crateriform liquefaction.

Agar colonies: Orange, small, convex, entire.

Agar slant: Orange, filiform, convex, slightly glistening, rugose.

Broth: Turbid with orange ring and sediment.

Litmus milk: Unchanged.

Potato: No growth. No acid or gas in dextrose, lactose, sucrose.

Starch: Not hydrolyzed.

Indol not formed.

Nitrates reduced to nitrites.

Nitrogen fixation: 1.3 mgm. in 100 gm. of soil.

Aerobic.

Optimum temperature: 25°C. to 30°C.

Habitat: Soil.

Micrococcus grammegans

Spheres: 1.0 to 1.5 μ , occurring in pairs and in clumps. Gram-negative.

Gelatin colonies: Small, grayish, punctiform, flat, entire.

Gelatin stab: Liquefaction stratiform.

Agar colonies: Small, cream-gray, circular, smooth, flat, entire.

Agar slant: Cream-gray, filiform, slightly raised, glistening, smooth, viscid.

Broth: Clear with scanty flaky sediment.

Litmus milk: Unchanged.

Potato: Gray filiform growth.

Starch: Hydrolyzed.

No acid or gas formed in dextrose, lactose, sucrose.

Indol not formed.

Nitrates not reduced.

Nitrogen fixation: 1.3 mgm. in 100 gm. of soil.

Aerobic.

Optimum temperature: 30°C.

Habitat: Soil.

Micrococcus indofaciens

Spheres: 1.0 to 1.5 μ , occurring in clumps. Gram-positive.

Gelatin colonies: Whitish, irregular, crateriform, entire.

Gelatin stab: Liquefaction crateriform.

Agar colonies: Whitish cream, circular, smooth, raised, entire.

Agar slant: Whitish cream, circular, smooth, raised, entire.

Broth: Turbid, with scanty flocculent sediment.

Litmus milk: Slightly acid becoming alkaline.

Potato: Steel-gray growth, media blackens.

Starch: Hydrolyzed.

No acid or gas formed in dextrose, lactose, sucrose.

Indol is formed.

Nitrates not reduced.

Nitrogen fixation: 2.7 mgm. in 100 gm. of soil.

Aerobic.

Optimum temperature: 30°C.

Habitat: Soil.

Micrococcus micans

Spheres: 1.0 to 1.5 μ , occurring singly, in pairs, and in clumps. Gram-negative.

Gelatin colonies: No growth.

Gelatin stab: No growth.

Agar colonies: Whitish-gray, large, circular, smooth, flat, entire.

Agar slant: Whitish-gray, abundant, filiform, flat, glistening, smooth, viscid.

Broth: Slightly turbid with scanty flaky sediment.

Litmus milk: Peptonized.

Potato: Grayish-cream growth.

Starch: Hydrolyzed.

No acid or gas formed in dextrose, lactose, sucrose.

Indol not formed.

Nitrates not reduced.

Nitrogen fixation: 3.05 mgm. in 100 gm. of soil.

Aerobic.

Optimum temperature: 25°C. to 30°C.

Habitat: Soil.

Micrococcus non-acidulus

Spheres: 0.5 to 1.0 μ . Occurring singly, in pairs, and in clumps. Gram-positive.

Gelatin colonies: No growth.

Gelatin stab: No growth.

Agar colonies: Whitish cream, large, circular, smooth, raised, entire.

Agar slant: Whitish cream, filiform, raised, glistening, smooth.

Broth: Flocculent turbidity, with abundant sediment.

Litmus milk: Peptonized.

Potato: Fairly abundant, grayish.

Starch: Hydrolyzed.

No acid or gas formed in dextrose, lactose, sucrose.

Indol not formed.

Nitrates not reduced.

Nitrogen fixation: 0.25 mgm. in 100 gm. of soil.

Aerobic.

Optimum temperature: 30°C.

Habitat: Soil.

Micrococcus subroseus

Spheres: 1.0 to 1.5 μ , occurring singly and in clumps. Gram-positive.

Gelatin colonies: No growth.

Gelatin stab: No growth.

Agar colonies: Pink, circular, smooth, raised, entire.

Agar slant: Abundant, pink, filiform, raised, glistening, smooth, viscid.

Broth: Turbid, with abundant flaky sediment.

Litmus milk: Unchanged.

Potato: Pale pink.

Starch: Hydrolyzed.

Acid in dextrose and sucrose.

Indol not formed.

Nitrates reduced to nitrites.

Nitrogen fixation: 2.7 mgm. in 100 gm. of soil.

Aerobic.

Optimum temperature: 30°C. to 35°C.

Habitat: Soil.

Micrococcus subfuscus

Spheres: 0.5 to 1.0 μ , occurring singly, in pairs, and in clumps. Gram-negative.

Gelatin colonies: Light brown, circular, flat, entire.

Gelatin stab: Liquefaction stratiform, and browned.

Agar colonies: Whitish cream, large, circular, smooth, slightly raised, entire.

Agar slant: Whitish cream, abundant, filiform, slightly raised, glistening, smooth, viscid.

Broth: Flocculent turbidity, with abundant sediment.

Litmus milk: Alkaline; peptonized.

Potato: Light grayish cream.

Starch: Hydrolyzed.

Acid in dextrose and sucrose; acid and gas in lactose.

Indol not formed.

Nitrates not reduced.

Nitrogen fixation: 8.1 mgm. in 100 gm. of soil.

Aerobic.

Optimum temperature: 30°C.

Habitat: Soil.

Penicillium chrysogenum, n. v.

Fructification with two stages, metulae and phialides. Metulae not inflated at the apex. Colonies velvety, greenish-gray, conidiophores 50 to 100 μ .

Gelatin stab: Liquefied and browned.

Agar slant: Greenish gray, abundant, dull, raised.

Broth: Ring, scanty, sediment.

Litmus milk: Peptonized.

Potato: Greenish-gray, abundant.

Starch: Hydrolyzed very slightly.

Acid formed in sucrose.

Indol not formed.

Nitrates not reduced.

Nitrogen fixation: 2.35 mgm. in 100 gm. of soil.

Optimum temperature: 25°C. to 30°C.

Habitat: Soil.

TABLE 1

Nitrogen fixation in 100 gm. of soil and optimum temperature of the organisms

NAME OF ORGANISM	NITROGEN FIXED AT 28°C. mgm.	OPTIMUM TEMPERATURE °C.
<i>Actinomyces albocinereus</i>	1.65	35
<i>Actinomyces cinereus</i>	2.70	35
<i>Actinomyces exfoliatus</i>	1.15	37
<i>Actinomyces fradii</i>	1.30	25 to 30
<i>Actinomyces filatosus</i>	0.60	35
<i>Actinomyces negrocinereus</i>	4.10	35
<i>Actinomyces negroflavus</i>	0.00	35
<i>Actinomyces roseus-purpureus</i>	5.85	35
<i>Actinomyces sphaerulorus</i>	2.70	35
<i>Actinomyces veundulatus</i>	2.70	35
<i>Bacillus annulofaciens</i>	1.30	30
<i>Bacillus aridii</i>	0.25	30
<i>Bacillus eviridi-pallens</i>	3.40	30
<i>Bacillus indolfaciens</i>	1.15	25 to 30
<i>Bacillus levanensis</i>	4.80	30
<i>Bacillus multumcrescens</i>	1.30	30
<i>Bacillus nephiti</i>	1.30	30
<i>Bacillus subfuscus</i>	2.70	30
<i>Micrococcus cinereus</i>	5.15	30
<i>Micrococcus conglomeratus</i>	1.13	25 to 30
<i>Micrococcus grammegans</i>	1.13	30
<i>Micrococcus indolfaciens</i>	2.70	30
<i>Micrococcus micanus</i>	3.05	25 to 30
<i>Micrococcus non-acidulus</i>	0.25	30
<i>Micrococcus subroseus</i>	2.70	30 to 35
<i>Micrococcus subfuscus</i>	8.10	30
<i>Penicillium chrysogenum</i>	2.35	25 to 30
All cultures together.....	9.70	
Nephi soil.....	11.60	

NITROGEN FIXATION

The nitrogen-fixing power of the isolated organisms was determined as follows: 20-gm. portions of dried, sieved soil of the same type as that from which the organisms had been isolated were placed in 500-cc. Kjeldahl flasks. To each flask 0.5 gram of mannite was added and the water content made to 20 per cent. They were then plugged with cotton, weighed, and sterilized in the autoclave for 4 hours at 15 pounds' pressure. Thorough sterilization of the soil was proved by plate tests.

The inoculum was prepared by inoculating the organism into tubes containing 5 cc. of Ashby mannite solution. After a good growth appeared the plugs and the tubes were flamed and the contents of the tube poured into the medium to be inoculated. The optimum water content was maintained during the incubation period by bringing it up to weight at regular intervals with sterile water. These, together with sterile blanks, were incubated for 21 days at 28° and then the total nitrogen was determined by the Kjeldahl method. All determinations were made in triplicate. The results are given in table 1.

It will be noticed that all but one organism, *Actinomyces negroflavus*, fixed nitrogen in the soil. These results are substantially the same as those of Emerson (3), who found 97 per cent of the soil organisms developing upon dextrose agar plates to be azofying bacteria. The nitrogen-fixing power of many of these organisms when in the soil is one third to one half of that reported for certain strains of the azotobacter (3). When inoculated in Ashley solution, however, practically all the cultures failed to fix nitrogen.

SUMMARY

1. Samples of soil were collected under sterile conditions from the Nephi Experimental Farm. These were plated and the colonies that developed upon Ashby mannite agar were obtained in pure culture.
2. Of the cultures isolated, 27 probably represent new species and varieties and are given in this paper.
3. A study of the morphological characteristics show 10 actinomyces, 8 bacilli, 8 micrococci, and 1 penicillium.
4. The study of the physiological activities indicates that 26 of the 27 are nitrogen-fixing organisms, ranging in nitrogen-fixing ability from 0.25 to 8.1 mgm.
5. Most of the cultures hydrolyze starch; out of 27 tested, 24 hydrolyze starch rather rapidly; 22 liquefy gelatin; 7 form indol; and 10 reduce nitrates to nitrites with varying ability. Nine cultures have optimum temperature from 35°C. to 37°C., 13 from 30° to 34°C., and 5 have optimum temperature below 30°C.

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PLATE 1

PREPARATIONS STAINED WITH CARBOL FUCHSIN

- FIG. 1. *Actinomyces albocinereus*. Beef extract agar. 5 days. $\times 800$.
- FIG. 2. *Actinomyces cinereus*. Beef extract agar. 5 days. $\times 1200$.
- FIG. 3. *Actinomyces exfoliatus*. Beef extract agar. 5 days. $\times 800$.
- FIG. 4. *Actinomyces filatosus*. Beef extract agar. 5 days. $\times 800$.
- FIG. 5. *Actinomyces negrocinereus*. Beef extract agar. 5 days. $\times 1200$.
- FIG. 6. *Actinomyces negrocinereus*. Beef extract agar. 5 days. $\times 1200$.
- FIG. 7. *Actinomyces negroflavus*. Beef extract agar. 5 days. $\times 800$.
- FIG. 8. *Actinomyces roseus-purpureus*. Beef extract agar. 5 days. $\times 800$.
- FIG. 9. *Actinomyces sphaerulosus*. Beef extract agar. 5 days. $\times 1200$.

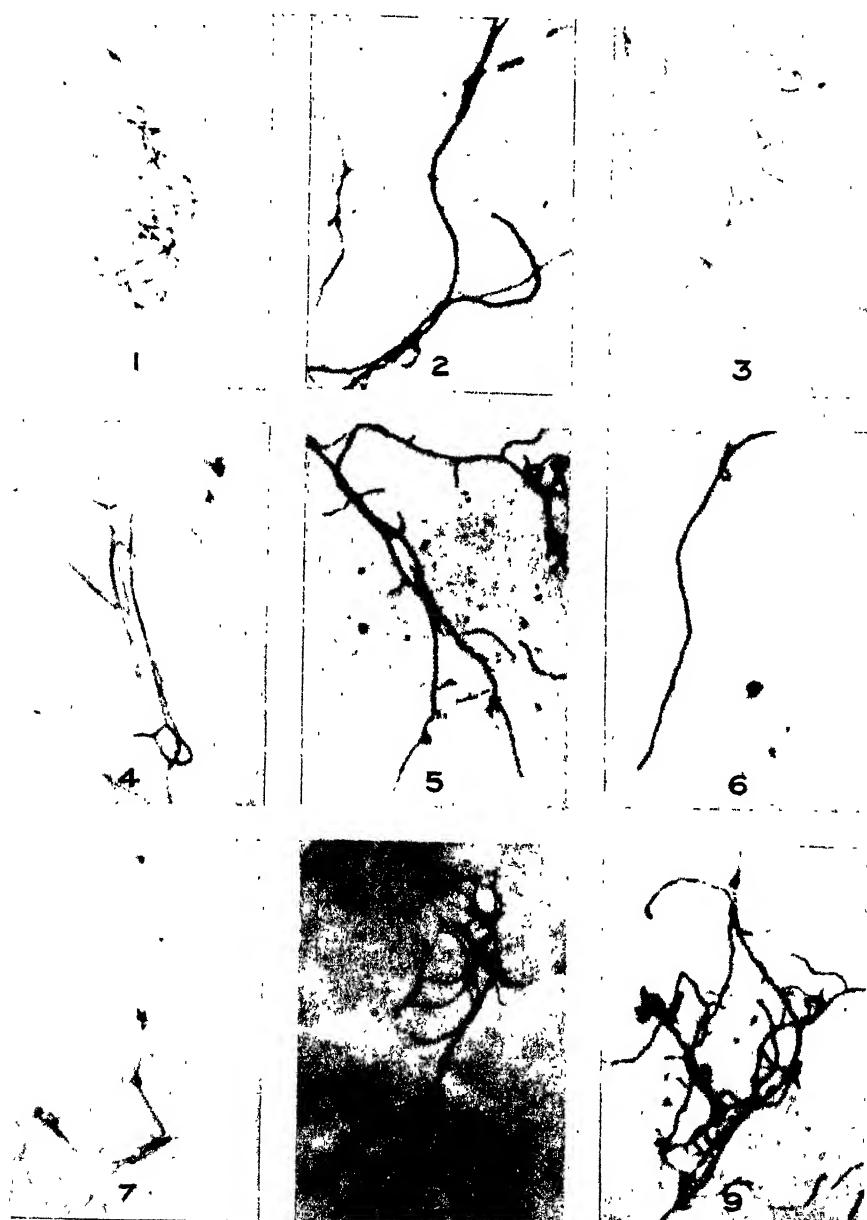


PLATE 2

FIG. 10. *Actinomyces veundulatus*. Beef extract agar. 5 days. $\times 800$.
FIG. 11. *Bacillus annulofaciens*. Beef extract agar. 2 days. $\times 1200$.
FIG. 12. *Bacillus aridii*. Beef extract agar. 2 days. $\times 1200$.
FIG. 13. *Bacillus eviridipallens*. Beef extract agar. 2 days. $\times 1200$.
FIG. 14. *Bacillus indolfaciens*. Beef extract agar. 2 days. $\times 1200$.
FIG. 15. *Bacillus levanensis*. Beef extract agar. 2 days. $\times 1200$.
FIG. 16. *Bacillus multumcrescens*. Beef extract agar. 2 days. $\times 1200$.
FIG. 17. *Bacillus nephii*. Beef extract agar. 2 days. $\times 800$.
FIG. 18. *Bacillus subfuscus*. Beef extract agar. 2 days. $\times 800$.

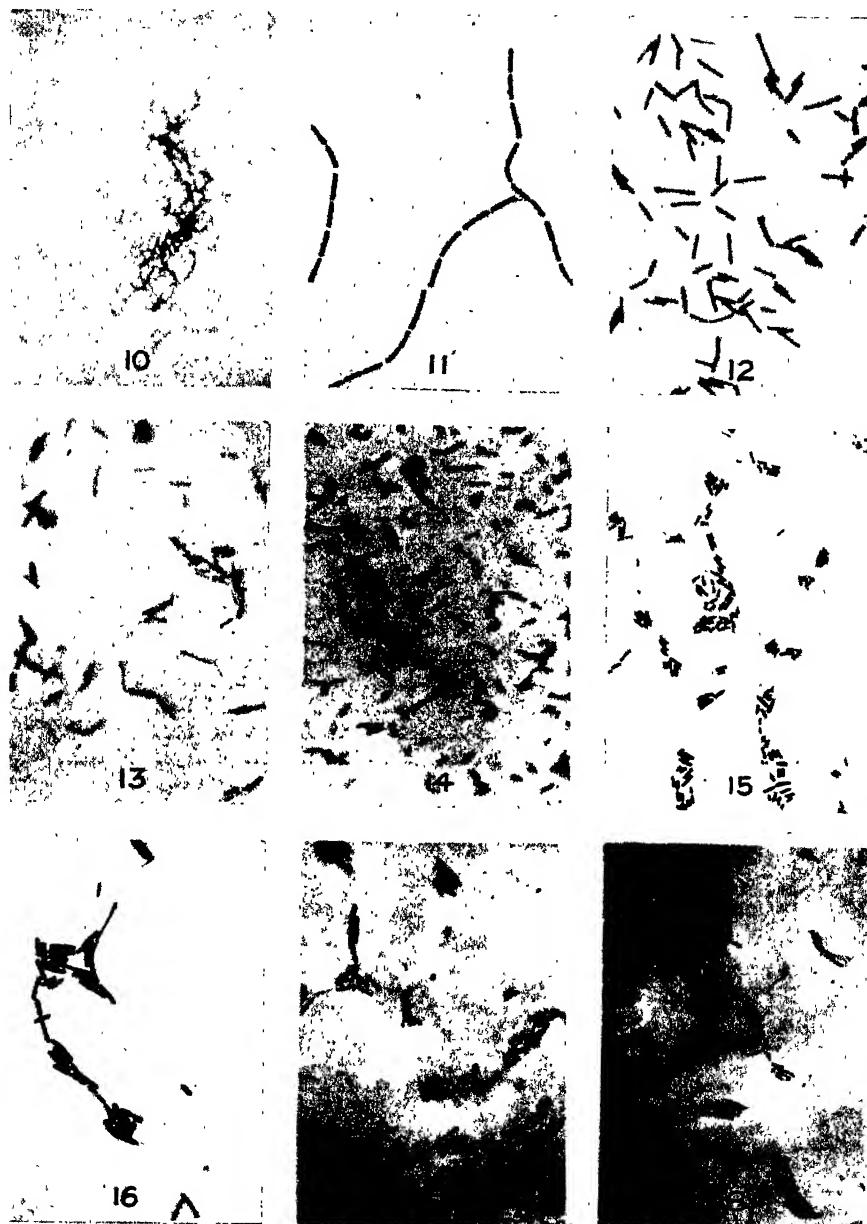


PLATE 3

FIG. 19. *Micrococcus cinereus*. Beef extract agar. 2 days. $\times 1200$.

FIG. 20. *Micrococcus conglomeratus*. Beef extract agar. 2 days. $\times 800$.

FIG. 21. *Micrococcus grannegans*. Beef extract agar. 2 days. $\times 1000$.

FIG. 22. *Micrococcus indolsaciens*. Beef extract agar. 2 days. $\times 1200$.

FIG. 23. *Micrococcus micans*. Beef extract agar. 2 days. $\times 800$.

FIG. 24. *Micrococcus non-acidulus*. Beef extract agar. 2 days. $\times 1200$.

FIG. 25. *Micrococcus subroseus*. Beef extract agar. 2 days. $\times 800$.

FIG. 26. *Micrococcus subfuscus*. Beef extract agar. 2 days. $\times 800$.

FIG. 27. *Penicillium chrysogenum*. Spores. Beef extract agar. 4 days. $\times 800$.



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FERTILIZER STUDIES WITH EARLY POTATOES¹

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The potato has held an important place in the human diet for a great many years. Its importance in this country can be realized from the yearly consumption of from 3.5 to 4.0 bushels per capita that has existed for several decades. More recently, however, its use as a stock feed and in the industries for the production of starch and alcohol, has appreciably increased the general consumption of the crop. It is obvious that the problems connected with the fertilization of the potato crop must grow in importance as the consumption increases. The purpose of this paper is to present the results of some extensive field studies, which were conducted in Maryland, on fertilizers for early potatoes with special reference to nitrogen and potassium.

REVIEW OF LITERATURE

In view of the importance of the potato in the human diet, it is quite natural to find reports of fertilizer experiments on this crop in early literature. However, as a rule the results of these earlier experiments have been, for the most part, rather indefinitely reported. For this reason the following review will be confined to some of the more recent work on the subject.

Whitney (18), in summarizing the results of potato fertilizer investigations conducted in 23 states, on a large number of soils and extending over a period of years, concluded that the actual increases in bushels of potatoes are larger with two or three fertilizer materials mixed than with single substances.

Truog et al. (14) compared the growth of potatoes in sand cultures supplied with complete nutrient solutions, with the nitrogen supplied from two mineral sources. They obtained the best growth with nitrate of soda and only poor growth with sulfate of ammonia. A mixture of the two materials, however, gave a fairly good growth. Attention was called to the importance of supplying nitrogen in several forms for field applications of fertilizer. It was pointed out that this practice would avoid a toxic effect from ammonical nitrogen, excess loss by leaching, and delay of early growth when only organics are used.

White (17), on the other hand, concluded that the poorest yields of potatoes were produced where nitrate of soda was used at the rate of 200 pounds per acre. This conclusion was based on the results of tests conducted at College Park and Ridgely, Maryland. Contrary to these results, Lipman and Blair (8) found that nitrate of soda gave larger yields of potatoes than equivalent amounts of sulfate of ammonia, fish, or tankage.

¹ Part 1 of a thesis submitted to the graduate faculty of the University of Maryland, June, 1928, in partial fulfillment of the requirements for the degree of doctor of philosophy.

Noer (9) compared activated sewage sludge with various organic and inorganic fertilizer materials as sources of ammonia in a complete potato fertilizer, and concluded that activated sewage sludge was a satisfactory source of nitrogen when used in this manner. It was also pointed out that activated sewage sludge exerted a favorable influence on the mechanical condition of the mixed fertilizers.

Russell (11) reported the results obtained with potatoes in a comparison of the newer nitrogenous fertilizers in Great Britain. He concluded that urea was of the same order of value as a fertilizer as nitrate of soda and sulfate of ammonia. It was pointed out that the use of urea had several distinct advantages: it does not wash out of the soil, does not puddle soils as does nitrate of soda, does not remove lime as does sulfate of ammonia, and makes a fertilizer mixture with good mechanical condition. Brown (4), conducted extensive experiments in various sections of the United States and compared the results obtained with organic and inorganic forms of nitrogen in the fertilizer mixture. Sulfate of ammonia gave better yields of potatoes than nitrate of soda in 9 out of 10 cases. When one-half of the ammonia was supplied from an organic source, there was an increase of 3.6 bushels obtained over the yield from the treatment containing only inorganic ammonia. In an earlier paper, Brown (5) summarized the results of some experiments with various nitrogen materials used in a complete fertilizer for potatoes in New York, Virginia, and Maine. Among other things he found that urea compared very favorably with nitrate of soda and sulfate of ammonia as a source of nitrogen for potatoes. In the same paper, were reported the results of 16 distinct experiments on different soil types over a period of years with three domestic potash materials. Muriate of potash, sulfate of potash, and Nebraska salts were used in complete mixtures containing 3, 5, and 7 per cent potash, 4 per cent ammonia, and 8 per cent phosphoric acid in each case. Very uniform yields of potatoes were obtained from all the treatments but muriate of potash gave uniformly better yields than the other two potash materials. The following results obtained by Brown (5) are given, since the comparative effects of muriate and sulfate of potash obtained, correspond closely with the results of the present potash studies that are presented elsewhere in this paper.

	3 per cent	5 per cent	7 per cent
Muriate of potash.....	234.7	240.4	245.1
Sulfate of potash.....	230.3	234.3	231.4
Nebraska salts.....	229.6	232.9	225.5

Starch determinations were made on samples of potatoes taken from the potash and no-potash plots. The results showed that muriate did not lower the starch content of potatoes in comparison with sulfate of potash. Furthermore, it is rather significant that no increase in starch content was found for the potatoes from the muriate plot in comparison with those taken from the no-potash plot. Zimmerly (20), has shown that in eastern Virginia, muriate of potash gave better yields of potatoes than did sulfate of potash. These results were obtained over a period of 3 years when 160 pounds of potash were applied per acre each year. However, when this amount of potash was doubled the increases for muriate were not uniform and the results indicated a slight toxic effect.

The work of Pate and Skinner (10) gave some evidence that ammonia and potash had more influence on the yields of potatoes than did phosphoric acid. However, the results as a whole showed that the best yields were obtained where a fertilizer containing nearly equal proportions of ammonia, phosphoric acid, and potash was used. The yields of potatoes were decreased when potash was withheld from the fertilizer mixture. Woods (19), studying the effects of omitting potash from the fertilizer used for potatoes in Maine, obtained a profitable increase in yields when 1500 pounds of fertilizer containing 3 per cent potash was applied. He also reported a beneficial effect on yields of potatoes when 300 pounds of sodium chloride were used per acre.

The average yields of potatoes obtained by Bergh (3) on a sandy loam soil with Irish Cobbler and Green Mountain varieties, show an increase of 60 bushels of marketable potatoes for

the potash plots over the yields from the no-potash plots. Increases for the potash applications were consistent where no stable manure had been applied. In other words, stable manure evidently helped to offset the effect of a fertilizer unbalanced with respect to potash.

Contrary to the results obtained by many investigators, Cooper and Rapp (6) found no beneficial effect on yields of potatoes from the use of potash in the fertilizer mixture. On the basis of returns per pound of fertilizer used, they ranked the fertilizer ingredients as follows: nitrogen, 2.08 bushels of potatoes; phosphoric acid, 1.605 bushels of potatoes; and potash, 1.23 bushels of potatoes. Wallace (16) found that potash manure salts did not give as high yields of potatoes as did muriate or sulfate of potash. He also noted that the leaves of the plants on all no-potash plots had a distinctly deeper green color than the leaves of the plants on the potash-treated plots. In this connection, Schreiner (12) has made a rather complete study of the symptoms associated with potash hunger of the potato plant. These he observed may be characterized by: dark green foliage, convex wrinkled leaf, drooping, and later exhibiting a bronzing effect. These symptoms were observed to be more marked in the potato fields on the sandy soils of the Atlantic Coastal Plain region. Potash hunger symptoms, as exhibited by the potato plant, are very characteristic and offer a fairly reliable guide in the fertilization of this crop.

In the foregoing review of literature, no particular mention was made of the effects of phosphoric acid on the potato crop. It is conceded that phosphoric acid is an essential ingredient of potato fertilizers in a large majority of cases, as already has been pointed out, but in compiling the literature for this review it was decided to confine the present discussion to the effects of nitrogen and potash in accordance with the experimental work described in this paper. In this work rate of fertilizer applications, especially with respect to nitrogen and potassium sources, and the subject of green manures, have all been carefully incorporated. The work was so planned and conducted throughout, as to conform as nearly as practicable with the best agricultural practices in the vicinity, in order that the results should be of practical as well as scientific value.

GENERAL PLAN OF EXPERIMENTS

The experimental plots were located 2 miles northeast of Snow Hill, Maryland. In this section of Maryland the predominating soils are the Norfolk, Sassafras, Elkton, and Keyport series. All are characterized by their low nitrogen, phosphoric acid, and potash content.

The topography in the vicinity of Snow Hill may be described as extremely flat, with the exception of an occasional sand hill, one of which extended along the western portion of the experimental area, including one entire series of plots.

The soil type used for the experiments was Norfolk sandy loam. This soil is especially low in nitrogen and potassium as may be seen from table 1, which shows the results of a mechanical and partial chemical analysis of a sample of the surface soil taken from the level portion of the experimental area. The subsoil appeared to contain more sand than the surface soil, hence the surface water was normally drained very rapidly.

Weather conditions. The 4-year average rainfall during the growing seasons

of the early potato crops amounted to 11 inches. The rainfall distribution in normal years was good. During the 1927 season the rain gauge at the field registered 2.72 inches for March, 2.88 inches for April, 1.72 inches for May, 2.85 inches for June, and 1.75 inches for July, making a total of 11.9 inches for the growing season. During the 1924 growing season, however, a total of 17.5 inches of rain was recorded, only 5.5 inches for 1925, and 10 inches for 1926.

A thermograph with the bulb placed 6 inches below the surface of the soil was used for recording the soil temperature during the growth of the crop. At the same time, the air temperature was recorded by the same instrument. The average mean soil temperature at a depth of 6 inches was 14.3°C. for the 1926 growing season, and 18.6°C. for the 1927 growing season. The average

TABLE 1
*Mechanical analysis**

	per cent
Fine gravel.....	1.2
Coarse sand.....	12.0
Medium sand.....	12.6
Fine sand.....	46.4
Very fine sand.....	8.2
Silt.....	15.3
Clay.....	4.4
Water-holding capacity.....	29.2
Total nitrogen.....	0.0766
Total potassium.....	0.8847
pH.....	6.4
Loss by ignition.....	2.3

* Mechanical analysis made by Bureau of Chemistry and Soils, U. S. Department of Agriculture.

mean air temperature for the same periods was 17.8°C. in 1926 and 15.5°C. in 1927.

Description and management of plots. The entire experimental area at Snow Hill consisted of approximately 5.2 acres. Of this area, 3 acres was used for early potato fertilizer experiments and the remainder was used for fertilizer experiments with sweet potatoes. The plots were 1/40 and 1/20 acre in size and were so arranged in series that the same crop and fertilizer treatments appeared on each plot every two years. This arrangement permitted a study of the accumulative effects of the fertilizer treatments. Early potatoes were rotated with sweet potatoes in every series, with a green manure cover crop on the land during the winter and early spring months. Where the effect of the green manure cover crop was studied, the land remained bare all winter.

The fertilizer treatments were applied with a one-row distributor illustrated in plate 1. This method of distribution thoroughly mixed the fertilizer with

the surface soil thus minimizing the possibility of fertilizer injury. The plots were marked out in 6 rows 30 inches apart and the fertilizer was applied about March 20 of each year. Planting followed as soon as possible after the fertilizer application. The seed potatoes were treated for scab, and cut as nearly as possible in pieces of 1.5 ounces as recommended by Appelman (1). Local grown seed of the Irish Cobbler variety was used throughout the work wherever early potatoes were grown. Planting was done with an Iron Age planter in the usual manner, except for the application of fertilizer, which was made as already described. Throughout the growing season, the control of insects was effected in the usual way with paris green or calcium arsenate. Practically no potato diseases were encountered at any time during the duration of the experiments.

About May 15 of each year, corn was drilled between every other row of potatoes so that 3 rows of corn were grown per plot in addition to the 6 rows of potatoes. At the time of harvesting the early potato crop, the corn was usually about 18 inches high and did not hinder harvesting operations.

The potatoes were harvested about July 10-15 each year. Digging was done in the manner customary in the locality by using a plow and later scratching out the potatoes by hand. All grading was done in the field using only two grades, U. S. grade No. 1, Primes, and culls. The weights of primes and culls were recorded in the field at digging time.

For convenience in discussing the results the data have been arranged in a number of series. These series are numbered consecutively and therefore do not necessarily correspond to the actual series numbers given in the field.²

Series 1. Influence of source of nitrogen in the fertilizer mixture

In this series various nitrogenous materials were compared to study their effect on yield of potatoes when used in a mixture containing 7 per cent ammonia, 6 per cent phosphoric acid, and 5 per cent potash. For all the treatments in this series and throughout the work to follow, unless otherwise designated, 16 per cent superphosphate was used as the source of phosphoric acid, and sulfate of potash as the source of potash. The basic fertilizer application for all treatments in this series was 2000 pounds per acre, in accordance with the usual practice where early potatoes are grown in this section. The yields of primes in bushels per acre for each year are shown in table 2 as well as the average yields of primes, the combined average yields of primes and culls, and the average percentage of culls for the 4-year period.

An examination of the data presented in table 2 will show distinctly the beneficial effect on yields of potatoes obtained from the use of organic nitrogenous materials in the fertilizer mixture. In all cases for the entire 4 years, the yields obtained where the nitrogen was derived from both organic and

² The yields for 1924 and 1925 were obtained by Dr. A. M. Smith. Those for 1924 were reported by him in a doctorate thesis, University of Maryland, June, 1925.

inorganic sources exceeded those where nitrogen was supplied only in the inorganic form. Where nitrate of soda was the only source of nitrogen, the yields of potatoes were consistently low and the average yield was the lowest obtained from any nitrogen treatment. These results would indicate that nitrate of soda, when used as the only source of nitrogen in the fertilizer mixture, is not a satisfactory nitrogenous material for early potatoes on this soil. Smith (13) showed that the losses of nitrate by leaching from Norfolk sandy loam are in proportion to the amount of nitrogen in the fertilizer mixture supplied from nitrate of soda. It would seem from this work and from the field results

TABLE 2
Influence of different nitrogenous materials and combinations in a 7-6-5 fertilizer on the yield of early potatoes

AMMONIA IN MIXTURE FROM	YIELD PER ACRE				AVERAGE		PER CENT CULLS (AVERAGE)	
	Primes				Primes	Primes and culls		
	1924	1925	1926	1927				
	bu.	bu.	bu.	bu.	bu.	bu.		
Nitrate of soda.....	68.0	25.0	121.0	118.0	83.0	116.0	28.4	
Sulfate of ammonia.....	87.5	37.0	154.0	145.0	106.0	133.0	20.3	
Dried ground fish.....	127.0	21.0	159.0	167.0	118.5	152.0	22.0	
0-6-5 no ammonia.....	22.0	19.0	103.0	12.0	39.0	69.0	43.5	
Packing house tankage.....	155.0	29.0	161.0	131.0	119.0	160.0	25.6	
$\frac{1}{2}$ nitrate, $\frac{1}{2}$ sulfate	114.5	32.0	114.0	149.0	102.4	137.0	25.2	
$\frac{1}{2}$ fish, $\frac{1}{2}$ tankage.....	147.0	22.0	164.0	134.0	117.0	157.0	25.4	
40 per cent inorganic,* 60 per cent organic†.....	144.5	26.0	174.0	152.0	124.1	156.0	20.4	
50 per cent inorganic, 50 percent organic.....	146.0	27.0	167.0	162.0	125.5	155.0	19.0	
60 per cent inorganic, 40 percent organic.....	133.0	20.0	167.0	170.0	122.5	154.0	20.4	
0-6-5 no ammonia.....	35.0	16.0	96.0	24.0	42.7	73.0	41.5	
70 per cent inorganic, 30 percent organic.....	170.0	25.0	155.0	158.0	127.0	157.0	19.1	
80 per cent inorganic, 20 percent organic.....	131.0	32.0	167.0	150.0	120.0	146.0	17.8	
Urea.....	39.0	187.0	173.0	133.0	164.0	18.9	
Activated sewage sludge.....	43.0	157.0	203.0	134.3	167.0	19.5	

* Inorganic = $\frac{1}{2}$ nitrate of soda and $\frac{1}{2}$ sulfate of ammonia.

† Organic = $\frac{1}{2}$ fish and $\frac{1}{2}$ tankage.

presented here, that the consistent low yields recorded for nitrate of soda were caused by a direct loss of nitrates from the feeding area of the crop. Sulfate of ammonia, on the other hand gave consistently better yields than nitrate of soda, but when the two materials were mixed, the average yield obtained was slightly lower than where sulphate of ammonia was used alone.

It is evident from the results obtained in table 2 that the different ratios of inorganic to organic nitrogen used in the mixture did not materially effect the yields of potatoes. From the results, the important consideration in this respect seemed to be the supplying of a part of the nitrogen in the mixture

from organic sources with a larger amount supplied from inorganic materials. Of the organic materials used, urea and activated sewage sludge gave the highest average yields, although these yields were calculated from the results of only 3 years. However, it may be seen from a comparison of the yields from these two materials in 1926 and 1927, that the yields from urea were more uniform than those from sewage sludge. As the season of 1925 was unusually dry, a comparison of the yields for that year does not seem warranted.

A further examination of the data given in table 2 will show conclusively that nitrogen was a limiting factor in potato production on this soil. The average yields of the check plots were less than 50 per cent of those obtained for any treatment, with one exception.

The average percentage of culls obtained for the treatments over the 4-year period showed no significant differences when various sources of nitrogen were used. However, there was a tendency toward a lower percentage of culls where organic nitrogen was used in the mixture. The percentage of culls for the check plots was almost double that obtained for the nitrogen-treated plots, with a few exceptions.

Series 2. Comparative effects of different organic and inorganic nitrogenous materials used in the mixture

This series of plots was planned principally to compare the relative effects of nitrate of soda, sulfate of ammonia, and Leunasalpeter when used in conjunction with organic materials as sources of nitrogen for potatoes. Several combinations and single sources of nitrogen suggested from the results of series 1 were also included in this series. The rate of application and the analysis of the fertilizer remained the same as in series 1, being 2000 pounds of a 7-6-5 mixture. Dried ground fish and packing house tankage in equivalent amounts were used to supply the organic portion of the mixture, except where urea was used. The yields of primes per acre, culls, and total yields for 1927 are shown in table 3.

From table 3 it may be seen that Leunasalpeter compared very favorably with nitrate of soda and with sulfate of ammonia in combination with fish and tankage. No significant differences in yields were obtained from the various combinations with urea, sulfate of ammonia, and nitrate of soda with fish and tankage. Leunasalpeter produced a larger yield of potatoes than urea where each was used as the only source of nitrogen in the mixture. However, the mechanical condition of the mixture containing Leunasalpeter as the only source of nitrogen, was so bad as strongly to discourage its use in this manner. On the other hand, the mixture containing urea was in excellent mechanical condition at the time it was applied to the soil. The relatively high yield of potatoes obtained in this series where nitrate of soda was used with organics, seems to further strengthen the evidence of the value of the use of organic as well as inorganic nitrogen materials in the mixture.

In an experiment of this kind, results from one year's work do not permit very definite conclusions to be drawn. However, the general conclusion that Leunasalpeter compared very favorably with nitrate of soda and sulfate of ammonia as a source of nitrogen for early potatoes, does seem warranted from the data presented.

Series 3. The effect of a green manure cover crop in addition to the fertilizer application

From the foregoing results it is evident that the sources of nitrogen in the fertilizer mixture constituted an important consideration in the fertilizer

TABLE 3

Comparative effects of different combinations of nitrogenous fertilizer materials on the yields of early potatoes for 1927

AMMONIA IN MIXTURE FROM	YIELD OF POTATOES PER ACRE		
	Primes bu.	Culls bu.	Total bu.
70 per cent nitrate of soda.....	211	27	238
30 per cent organic*.....			
70 per cent sulfate of ammonia.....	192	23	215
30 per cent organic.....			
70 per cent leunasalpeter.....	193	18	211
30 per cent organic.....			
50 per cent urea.....			
30 per cent sulfate of ammonia.....	175	19	194
20 per cent organic.....			
20 per cent nitrate of soda.....			
50 per cent sulfate of ammonia.....	175	18	193
30 per cent organic.....			
Urea.....	149	23	172
Leunasalpeter.....	169	23	192

* Organic $\frac{1}{2}$ fish and $\frac{1}{2}$ tankage.

problem involved in the production of early potatoes on Norfolk sandy loam. However, the potato crop probably was not capable of utilizing all of the fertilizer applied each year. This would mean that the residual effect from the fertilizer would be considerable, unless losses occurred by leaching. It is probable, however, that losses of nitrates, especially, took place rapidly. Hence, the problem of conserving that portion of the fertilizer not utilized by the crop was presented. Intercropping with corn undoubtedly helped to reduce these losses, but an additional reduction was effected by growing a green

manure cover crop of rye and vetch on the land during the winter and early spring. Not only should a green manure cover crop conserve the residual fertilizer remaining after the potato crop was removed, but it in turn should considerably increase the amount of organic matter added to the soil each year. In order to study the effectiveness of a green manure cover crop in these respects, a series of 7 plots was conducted. These plots received fertilizer treatments identical with 7 of the treatments used in series 1, except that in this case all the plots were allowed to remain bare during the winter and until sweet potatoes were planted the following year. Corn was planted between the rows

TABLE 4

Effect of a green manure cover crop in addition to fertilizer treatment on yields of early potatoes

AMMONIA IN MIXTURE FROM	YIELD PRIMES PER ACRE			3-YEAR AVERAGE
	1925	1926	1927	
	bu.	bu.	bu.	bu.
Nitrate of soda.....	25.0	121.0	118.0	88
Nitrate of soda plus green manure.....	52.0	116.0	193.0	120
Sulphate of ammonia.....	37.0	154.0	145.0	112
Sulphate of ammonia plus green manure.....	63.0	140.0	175.0	126
Dried ground fish.....	21.0	159.0	167.0	116
Dried ground fish plus green manure.....	64.0	176.0	191.0	144
40 per cent inorganic, 60 per cent organic*.....	26.0	174.0	152.0	117
40 per cent inorganic, 60 per cent organic plus green manure.....	59.0	165.0	204.0	143
50 per cent inorganic, 50 per cent organic.....	27.0	167.0	162.0	116
50 per cent inorganic, 50 per cent organic plus green manure.....	64.0	152.0	199.0	138
60 per cent inorganic, 40 per cent organic.....	20.0	167.0	170.0	119
60 per cent inorganic, 40 per cent organic plus green manure.....	71.0	131.0	226.0	143
70 per cent inorganic, 30 per cent organic.....	25.0	155.0	158.0	113
70 per cent inorganic, 30 per cent organic plus green manure.....	62.0	146.0	225.0	144

* Organic = $\frac{1}{2}$ fish and $\frac{1}{2}$ tankage. Inorganic = $\frac{1}{2}$ sulfate of ammonia and $\frac{1}{2}$ nitrate of soda.

of early potatoes on these plots as was done on series 1. For comparison, the yields of prime potatoes for 1925, 1926 and 1927 are shown in table 4 together with the average yields for the 3-year period.

From a consideration of the data presented in table 4 it is apparent that the green manure cover crop did not show a consistent increased yield in 1926. However, the yields for 1925 and 1927 show striking increases in yields for the green manure plots over those obtained for the no-green manure plots. This yearly variation in the results may be explained by the fact that in 1925 and 1927 the plots receiving green manure treatment were located on the sandy hill extending along the west side of the experimental area. In 1926, however,

the plots receiving a green manure cover crop were located on a practically level portion of the field where the soil was in a somewhat higher state of fertility. In 1924 the plots were located on the level portion of the field but the yields for this year are not given since this was the first year of the experiment and no green manure had been grown the previous winter. It should be noted further that the plots receiving no green manure were located on level land during the entire four years of the experiment. The yields for the green manure and no-green manure plots are, in one sense, not comparable in 1925 and 1927, as a comparison for these years accentuates the returns for green manure. On the other hand, a comparison of the yields for these years is interesting since it brings out the relative increases that may be expected from green manures when used in conjunction with fertilizer applications on the sand hills that occur in this section.

The occurrence of decreases in yields of potatoes where a green manure crop was used in 1926 is rather hard to explain. These decreases, however, may have been caused by a retardation of bacterial action in the soil brought about by the plowing under of the green manure in the spring. This in turn may have retarded the nitrification of the organic materials added in the fertilizer. The extent of this action would, of course, depend on the quantity of green manure plowed under and on the nitrogen-carbon ratio of both the soil and the green manure.

In consideration of the results obtained for 1925 and 1927, especially for the latter year, since 1925 was an unusually dry year, it is especially noteworthy that the yields of potatoes were increased in every case where a green manure crop was used, even though these plots were located on the sandy hill. The results from the use of a green manure crop under these soil conditions were undoubtedly very largely brought about by the fertilizer residues remaining in the soil after the sweet potatoes had been dug the previous year. Without this residual fertilizer, it is very probable that the results would not have been so satisfactory, since the green manure crop in this case would undoubtedly have made a very poor growth.

Series 4. Rates of fertilizer applications and the value of inorganic nitrogen applied at planting time in relation to yields of early potatoes

The fertilizer used in this series contained 7 per cent ammonia, 6 per cent phosphoric acid, and 5 per cent potash applied at the different rates shown in table 5. The nitrogen in the mixture was derived from equivalent amounts of nitrate of soda, sulfate of ammonia, dried ground fish, and packing house tankage. Phosphoric acid and potash were supplied from the same sources as in the previous series. The usual procedure was followed throughout in applying the fertilizer, 75 per cent being applied at the time of planting the potatoes and the remaining 25 per cent at the first cultivation of the crop. However, for one treatment at each rate of application, except for the highest rate, only organic nitrogenous materials were contained in the portion of the

mixture applied at planting-time. In these cases, the remainder of the mixture, containing only nitrogen derived from nitrate of soda and sulfate of ammonia, was applied at the first cultivation. At each rate of application the total amount and analysis of fertilizer were the same, the only difference being the time at which the inorganic nitrogen was applied. The yields of early potatoes produced in 1927 on these plots expressed in bushels per acre together with the average yields obtained in 1926 and 1927 from the rate-of-application plots are given in table 5. The study made on the effect of deferred inorganic nitrogen application was begun in 1927, consequently only one year's results are given for this work.

The data presented in table 5 show that there was a decrease in yields of potatoes in every case where the application of soluble inorganic nitrogen was

TABLE 5
Effect of deferring the inorganic nitrogen application and effect of rate of application on yields of early potatoes

POUNDS 7-6-5 FERTILIZER PER ACRE	YIELDS OF POTATOES PER ACRE	
	1927	Average, 1926-27
No fertilizer	bu.	bu.
1,000	17	17.5
1,000*	151	127.0
1,500	123
1,500*	219	187.0
2,000	152
2,000	217	180.0
2,000*	205
No fertilizer	51	35.5
2,500	268	222.5
2,500*	211
3,000	253	215.5

* Indicates deferred inorganic nitrogen application.

deferred until the potatoes were cultivated. The yields were consistently lower for these plots even at the higher rates of application. During the growing season there was very little difference noticeable in the appearance of the potato vines on the plots differently treated with respect to the nitrogen application. However, it seems apparent from the yields obtained, that the utilization of available nitrogen at the earliest growth of the potato plant is an important consideration in fertilizing this crop. Although the results obtained are for one year only the consistency of the results is very significant.

In considering the average yields of the potatoes produced on the rate-of-application plots for 1926 and 1927, it would seem that the 1500-pound application was the most profitable rate. However, the actual value of the applications cannot be determined unless the cost of the fertilizer used and the prices received for potatoes are given consideration. This phase of the problem offers a very interesting economic study for further work.

Series 5. A comparison of varying amounts of different potassium materials used in the fertilizer mixture for early potatoes

An extensive series of plots 1/40 acre in size was laid out in 1927 for the purpose of studying the relative effects of muriate of potash, sulfate of potash, and manure salts (20 per cent) on the yields of early potatoes. The three materials were sued to supply equivalent quantities of potash amounting to 5, 8, and 10 per cent in mixtures containing, in each case, 7 per cent ammonia and 6 per cent phosphoric acid. Seventy per cent of the ammonia in the mixture was derived from equivalent amounts of nitrate of soda and sulfate of ammonia, and 30 per cent from equivalent amounts of dried ground fish and packing house tankage. The phosphoric acid was supplied by 16 per cent superphosphate as usual.

To eliminate soil variations, the treatments were replicated twice and the replicate plots were distributed systematically over the field. The entire arrangement of the plots was repeated in an adjoining field for a similar study with sweet potatoes. By this arrangement, a rotation of early potatoes with sweet potatoes was made possible without varying the potash treatment on any one plot for either crop. Moreover, a study of the residual effects of the treatments was also made possible. The experiment was conducted in the same manner as the previous series, corn being used as an intercrop with rye and vetch for a green manure cover crop during the winter. The average yields of potatoes produced on the triplicate plots for 1927 are given in table 6 together with the average yields of four check plots.

The results obtained from the different treatments for 1927 are not conclusive as to the value of the different potash materials for early potatoes. At best, the first year of an experiment of this kind with potash materials can only be expected to give an indication of the results that may be obtained after a longer period. Accordingly, the results will be discussed on this basis.

One of the outstanding points of the experiment was the larger average yields of potatoes obtained where potash was used in comparison to the yields obtained where no potash was used. Evidently, potash as well as nitrogen is needed to obtain maximum yields of potatoes on this soil. The yields obtained from the check plots over a period of years should be very interesting from a plant nutrition standpoint. Although the check plots gave an average yield of 124 bushels for 1927, yet the plants on these plots exhibited typical potash hunger symptoms, especially during early growth. The leaves were small, curled, and dark green almost shading into purple in some instances. As early as 1867, such leaf coloration was known to be associated with potash-hunger. In this year Voelcker (15) noted the dark green color of the leaves of mangolds grown on land where no potash salts were applied. The color of the leaves of the potato plants growing on the plots variously treated with respect to potash in the present experiment, corresponded very closely to the color variations observed by Voelcker (15) with mangolds. The lightest leaf

coloration was observed on the plots receiving manure salts. The cause of this gradation of leaf color with different potash treatments offers a very interesting study in plant nutrition.

A point of interest brought out by an examination of the data given in table 6 is the lower average total yields obtained where manure salts were used in the mixture in comparison to the yields obtained with muriate or sulfate of potash. This effect of manure salts may have been a direct or an indirect osmotic effect on the young potato plants. The sodium chloride applied with the manure salts may have retarded the nitrification of the organic materials applied in the fertilizer, and thus affected the yields indirectly. This subject will be treated at length in a later paper.

From a further examination of table 6 it would seem that the potash materials may be arranged in the following order in relation to the increases in yields obtained over the check plots: first, muriate of potash; second, sulfate of

TABLE 6

Yields of early potatoes when various potassium materials were used in different amounts in the fertilizer mixture

POTASH IN MIXTURE FROM	AVERAGE YIELDS PER ACRE OF TRIPPLICATE PLOTS								
	7-6-5			7-6-8			7-6-10		
	Primes	Culls	Total	Primes	Culls	Total	Primes	Culls	Total
	bu.	bu.	bu.	bu.	bu.	bu.	bu.	bu.	bu.
Manure salts (20 per cent).....	199	23	222	200	22	222	224	14	238
Muriate of potash.....	225	21	246	209	28	237	226	20	246
Sulfate of potash.....	211	20	231	196	25	221	209	28	237
No potash 7-6-0*.....	124	29	153

* Average yields of 4 check plots.

potash; third, manure salts. It also may be noted from table 6 that no significant increases in yields of prime potatoes were obtained for any of the potash materials when applied in amounts above the equivalent to 5 per cent potash. These results are in accord with those obtained by Johnston (7) and others.

Total starch determinations by the Official acid-hydrolysis method (2) were made on several samples of the potatoes from different plots. The samples taken from the check plots receiving no potash showed the same starch content as the samples of potatoes taken from the plot receiving a 7-6-10 fertilizer with the potash from sulfate.

Series 6. Effect of a double strength fertilizer applied at half the usual rate

Two fertilizer mixtures were made up for this experiment, one containing 14 per cent ammonia, 12 per cent phosphoric acid, and 10 per cent potash and the other containing the same amounts of ammonia and potash but only half the amount of phosphoric acid. The rate of application was 1000 pounds

per acre. The ammonia in the mixtures was derived entirely from urea, the phosphoric acid from 20 per cent superphosphate, and the potash from sulfate of potash. The yields of potatoes in bushels per acre produced in 1927 on 1/40-acre plots where these treatments were applied are given in table 7.

These plots adjoined those of series 2, therefore a comparison of the yields given in table 7 with those in table 3 can be made. Such a comparison shows that the 14-12-10 mixture, applied at the rate of 1000 pounds per acre, compared very favorably with the 7-6-5 mixtures applied at double that rate. However the 14-6-10 mixture at 1000 pounds per acre produced a slightly lower yield of potatoes than was obtained with the 14-12-10 mixture. It would seem from the results for 1927 with concentrated mixtures, that no damage was caused to the crop by their use. If the rate of application of concentrated mixtures is made commensurate with the increase in analysis as compared with the 7-6-5 mixtures, there will probably be little danger from fertilizer injury.

TABLE 7
Yields of early potatoes obtained with concentrated mixtures

ANALYSIS	RATE PER ACRE	YIELD POTATOES PER ACRE		
		Primes	Culls	Total
	lbs.	b <u>u.</u>	b <u>u.</u>	b <u>u.</u>
14-12-10	1,000	208	24	232
14-6-10	1,000	192	28	220

SUMMARY OF RESULTS

A comparison of different forms of nitrogen in a 7-6-5 fertilizer mixture used for early potatoes indicated the value of deriving a part of the nitrogen from organic sources.

Leunasalpeter compared very favorably with nitrate of soda and sulfate of ammonia as a source of inorganic nitrogen in the fertilizer mixture but the mechanical condition of the mixture was extremely bad.

Potato yields obtained on a sand hill were increased where a green manure cover crop of rye and vetch was grown the preceding winter and early spring.

The yields of potatoes were lowered when the soluble mineral nitrogen portion of the fertilizer mixture, usually applied at planting time, was omitted and its application deferred until the first cultivation of the crop.

In every case plots receiving potash gave higher average yields of potatoes in comparison to the average yields produced on the no-potash plots. A comparison of the potash materials used showed muriate, first; sulfate, second and manure salts, third, from the standpoint of yields produced.

With respect to yields of early potatoes produced, double strength fertilizers applied at half the usual rate compared favorably with the regular 7-6-5 mixtures applied at 2000 pounds per acre.

CONCLUSIONS

1. A portion of the ammonia in the fertilizer mixture for early potatoes grown on Norfolk sandy loam should be supplied by organics. A larger portion of the ammonia should be supplied from inorganic than from organic materials.
2. A green manure cover crop of rye and vetch used in the regular fertility program on light sandy soils where commercial fertilizers are applied, will help to conserve the fertilizer residues and to increase yields.
3. One year's results show that applications of potash are needed to obtain maximum yields of early potatoes on this soil and that either muriate or sulfate of potash is preferable to manure salts when applied on the basis of equivalent amounts of potash in a complete fertilizer mixture.

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PLATE 1

ONE-ROW FERTILIZER DISTRIBUTOR USED FOR APPLYING ALL FERTILIZER TREATMENTS



A NOTE ON THE DETERMINATION OF THE VOLUME-WEIGHT OF DIFFERENT SOILS IN THE SOIL PROFILE

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In a recent paper Lebedev (2) described a new type of soil sampler for the determination of the volume-weight or apparent specific gravity of soils. He pointed out the advantages of presenting data on soil analysis from the standpoint of volume-weight rather than from the actual weight of the soil.

The idea of apparent specific gravity or volume-weight, of course, is not new. In the classical work of the savant of the American school of soil science, the late Doctor Hilgard, the determination of the volume-weight has been recognized and a discussion may be found in his book (1).

The new sampler of Lebedev has been tried out at the New Jersey Station in connection with a series of extensive studies on the soil profile of the soils in New Jersey. It was found that in profile studies, the A₀ horizon—the leaf mould of virgin soils—does not lend itself to sampling with this sampler.

Another difficulty encountered was the sampling of soils containing pebbles. The pebbles obscured the true volume of the soil, and the determinations made on such soils with the sampling tube could not be used.

Although pebbles in a soil are an integral part of the soil mass, their weight or volume does not enter into the chemical and biological or even most of the physical properties of the soil material itself. It is important, however, to determine the true, or more accurately speaking, the active volume of the soil in order to interpret properly the various soil phenomena. It was then necessary to evaluate the pebble factor in the determinations of the volume-weight of soils.

In order to get around this difficulty the following procedure is followed: Three or four samples of the soil are taken from each horizon on a freshly dug soil profile cut with the sampling tube described by Lebedev. The soil is placed into tared aluminum dishes, tightly covered, and weighed as soon as it is brought to the laboratory. The dishes are then opened and placed in an electric oven and the soil dried at 100–105°C. for 12 hours or more to constant weight. The soil is then removed, sifted through a 2-mm. sieve, and the weight and volume of the mineral debris are determined in the following manner:

From a series of determinations on the debris of several soil types it was

found that by taking their specific gravity as 2.6¹ the volume calculated checked very well with the volume obtained by the displacement method. The volume of the debris is subtracted from the volume of the sampling tube, the weight of the debris subtracted from the dry weight of the sample, the new weight divided by the new volume, and the quotient taken as the *active volume-weight*. The following example taken from a larger number of determinations

TABLE 1
Volume weight of soils containing pebbles

LABORATORY NUMBER OF SAMPLE	HORIZON IN SOIL PROFILE	DRY WEIGHT OF SOIL FROM SAMPLER BEFORE SIFTING	WEIGHT OF SOIL AFTER SIFTING THROUGH A 2-MM. SIEVE	WEIGHT OF DEBRIS	VOLUME OF DEBRIS	VOLUME OF SOIL WITHOUT DEBRIS*	ACTIVE VOLUME-WEIGHT OF SOIL
		gm.	gm.	gm.	cc.	cc.	

Gloucester gravelly loam

35	A ₁	22.9	22.400	0.500	0.19	27.51	0.814
35	A ₁	26.2	24.825	1.375	0.53	27.17	0.914
35	A ₁	24.8	24.375	0.425	0.16	27.54	0.850
36	A ₂	30.4	29.150	1.250	0.48	27.22	1.071
36	A ₂	32.9	31.250	1.650	0.64	27.06	1.154
36	A ₂	33.8	32.200	1.600	0.63	27.07	1.182
37	B ₁	37.3	32.340	4.960	1.90	25.80	1.253
37	B ₁	35.8	34.860	0.940	0.36	27.34	1.275
37	B ₁	36.8	35.540	1.260	0.50	27.20	1.306
38	B ₂	40.9	37.750	3.150	1.21	26.49	1.424
38	B ₂	38.2	36.530	1.670	0.64	27.06	1.349
38	B ₂	39.5	36.140	3.360	1.30	26.40	1.369

Dover loam

42	A ₃	40.0	35.56	4.44	1.7	26.0	1.37
42	A ₃	39.2	34.80	4.40	1.7	26.0	1.34
42	A ₃	36.6	34.52	2.08	0.8	26.9	1.30
43	B ₁	39.5	36.2	3.30	1.3	26.4	1.37
43	B ₁	42.0	37.88	4.12	1.6	26.1	1.45
43	B ₁	43.6	36.59	7.01	2.7	25.0	1.46

* The volume of the sampling tube is equal to 27.7 cc.

illustrates the procedure. It also shows the accuracy of the method of the volume-weight sampler used.

The data given, aside from illustrating the method of getting at the true volume-weight, show how the volume-weight increases with the depth in the soil profile. How this would influence the analytical figures of the physical, chemical, and biological data and their interpretation may be judged from the following example: soil 36 contains 25.1 per cent H₂O, soil 37 contains 24.1

¹ The specific gravity of the pebbles may be determined in each case by the balance method, using either a platinum or horse-hair basket.

per cent. The average volume-weight of soil 36 (the average of 3 samplings) is 1.136; of soil 37—1.278. Taking the area of one acre (4047 square meters) and a depth of 10 cm., soil 36 will have 404.7 cubic meters of soil or 404,700,000 cc. Its volume-weight being 1.136, its weight is 459,739 kgm.; its moisture content being 25.1 per cent, the total moisture in it is 115,394.5 kgm. Taking soil 37 at the same depth, we find that its weight is 517,206 kgm. and the total moisture content is 124,646 kgm., or 7 per cent more moisture than soil 36 which has a higher percentage of moisture.

A determination of the active volume-weight of soils as defined is important inasmuch as it gives an accurate picture of the sphere of activities in the soil mass. The pebbles of the different rocks have no immediate value for the soil mass; they are a remote potential source of the soil mass.

The active volume-weight of soils may be represented by the following formula: $V_a = \frac{w - w_1}{v - v_1}$, where V_a = the active volume-weight, w = the weight of the dry soil as taken with the sampling tube, w_1 = weight of pebbles not passing a 2-mm. sieve, v = volume of sampling tube (27.7 cc. in our case) and v_1 = the volume of the pebbles calculated by dividing their weight by the specific gravity, which may be determined in each case, or the value 2.6 taken as an average for the specific gravity of rock pebbles found in soils.

For soils which have no pebbles, w_1 and v_1 equal zero, e.g. the dry weight of the soil from the sampler divided by the volume of the sampler gives the active volume-weight.

This note is presented as a preliminary account; more work is being done and will be presented as the data accumulate.

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THE VALUE OF NITRIFICATION TESTS ON SOILS REPRESENTING EXTREME CONTRAST IN PHYSICAL AND CHEMICAL PROPERTIES¹

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In making nitrification tests in soil, it must be recognized that biological phenomena involved may be radically influenced by the amount and kind of chemicals used and the physical and chemical characteristics of soil employed in making the test. Parallelism between the nitrifying powers of soils and their crop-producing powers so frequently reported are remarkable when we consider the wide range of conditions under which these tests have been made. Investigations, where sterile liquid culture media have been inoculated with equal quantities of soil, have shown that soil treatments do cause biological changes which have resulted in increased efficiency of the nitrifying flora.

The use of fresh soil for nitrification tests to which has been added equal quantities of ammonium sulfate, blood meal, or some other nitrogenous compounds, however, introduces the physical and chemical conditions peculiar to the soil. These conditions may be so extreme that differences in the physiological efficiency of the organisms could hardly be detected. For example, Kelley (4) found that practically no effects were produced by adding infusions from cultivated to uncultivated soils, or vice versa, except where dried blood and lime were added also, and the author (1) has shown that the factors which determine the nitrifying power of a silty clay loam are not transmitted to a similar soil having a lower nitrifying power by inoculating this soil with a soil infusion.

It would be expected that heavy colloidal soils in which aeration is slow would likewise be slow to show accumulation of nitrates as compared to sandy soils containing a less vigorous nitrifying flora. This condition has limited the promiscuous use of nitrification tests, so that they are now used mainly for comparing the effects of various treatments upon the same type of soil used, and every soil type with its particular biological, chemical, physical, and regional climatic conditions must be regarded as an individual problem. Sandy soils from humid regions would hardly be expected to nitrify ammonium sulfate unless some basic materials were added, and, on the other hand, one

¹ Contribution from the Oregon Agricultural Experiment Station. Published with the approval of the director and the experiment station committee on soils.

² Associate bacteriologist. The author is indebted to Harold W. E. Larson for some of the determinations reported in this paper.

could hardly expect alkaline sandy soils to nitrify quantities of blood meal or casein in excess of a normal field application. In fact Waksman (6) says,

When we compare the nitrifying capacity of two soils by the common method of adding ammonium sulfate (much in excess of what we would add to field soils) to 100 gm. of soil and determining the nitrates formed after incubation, we actually measure not the nitrifying capacities of the two soils but merely, in a round-about way, the initial reaction, buffer content, and presence of neutralizing substances of the soil.

That the conditions under which these nitrification tests are made may materially influence results obtained is shown by Kelley (5) who found that the amount of nitrate formed from dried blood, bone meal, or ammonium sulfate during 4 weeks incubation varied enormously when different concentrations were used. He points out that widely different conclusions may be drawn from laboratory experiments when different periods of incubation are used. He suggests the use of quantities of nitrogenous materials comparable with those that obtain in the field.

Harper and Boatman (3) also found that a higher percentage of nitrate nitrogen was produced from small applications of ammonium sulfate than from larger applications, and, in most cases, a fairly good agreement occurred between the soil reaction and its nitrifying power when 100 mgm. of ammonium sulfate was added to 100 gm. of soil and incubated for 28 days. However, when 30 mgm. of ammonium sulfate was used in place of 100 mgm. and incubated with 100 gm. of soil for 15 days, it was found that the nitrifying power of the acid soils used was as great as that of the neutral or basic soils tested. In studying the residual effect of alfalfa on the nitrifying power of a Carrington loam, Harper and Boatman found no difference in the rate at which a 30 mgm. addition of ammonium sulfate was nitrified though some of the plots were strongly acid and had received no treatment, while others had received manure, limestone, and acid phosphate in different combinations. Other check plots which had not grown alfalfa had a very low nitrifying power.

After making a careful study of nitrification on plots of varying fertilizer and crop history using different methods and modifications, Waksman (6) concludes that, in order to get a thorough idea of the nitrifying capacity of the soil and have a basis for comparing the nitrification of different soils, no one single method is sufficient but a combination of methods is recommended, all of which should be used for each soil and each of which gives some information necessary to obtain a complete picture of nitrification in the soil. He recommends that nitrification be run in solution as recommended by Remy, Löhnis, and others; nitrification of the soil's own nitrogen, nitrification of ammonium sulfate in the soil [30 mgm. N as $(\text{NH}_4)_2\text{SO}_4$] per 100 gm. of soil, nitrification of ammonium sulfate in the soil in the presence of a theoretical amount of calcium carbonate [210 mgm. of CaCO_3 and 30 mgm. N as $(\text{NH}_4)_2\text{SO}_4$], and nitrification in the soil of organic nitrogenous materials (dried blood 0.1 per cent). By giving definite weight to the information

obtained by each of these five methods, a true picture of nitrification in soil may be obtained.

PURPOSE OF THIS INVESTIGATION

The purpose of this investigation is to make a comparison of the nitrifying powers of the fertilizer plots on two of the experimental tracts maintained by the Oregon Agricultural Experiment Station. The soils of these tracts represent extreme variations in physical and chemical properties.

The plots at the Corvallis Station are located on well drained Willamette silty clay loam, which is a dark soil well supplied with organic matter and has normally a hydrogen-ion concentration approximating pH 5.3. These plots have been under fertilizer treatment since 1914.

The plots of the Hermiston Station are located on Umatilla medium sand which, being light and arid, is naturally deficient in organic matter and plant-food. This soil has a normal hydrogen-ion concentration approximating pH 7.2. These plots had been in fertilizer treatment for only three years.

The extreme contrast in the physical conditions of these soils should prove the value of nitrification tests in demonstrating residual effects of fertilizer applications.

EXPERIMENTAL

In determining the nitrifying powers of these soils, only modifications of the soil method were used. The solution method might have yielded valuable data but, since the physiological efficiency of the nitrifying flora is of secondary importance to the physical and chemical conditions in determining the nitrifying power of the soil, the solution method would be of little or no practical value in establishing the merits of this method under such widely varying physical and chemical conditions.

The modifications of the soil method used were:

1. Nitrification of the soil's own nitrogen, 100 gm. of soil in the laboratory for 28 days under optimum moisture conditions;
2. Nitrification of ammonium sulfate in soil; 30 mgm. of nitrogen as ammonium sulfate incubated for 28 days as in 1;
3. Nitrification of ammonium sulfate in the presence of 210 mgm. of calcium carbonate;
4. Nitrification of organic nitrogenous materials; 0.1 per cent of blood meal, period of incubation 28 days in laboratory as in above tests.

Table 1 shows the fertilizer treatments that have been made on Willamette silty clay loam plots once in each 3-year rotation since 1914.

Figure 1 is a graphic presentation of these results. A glance at these data shows that the nitrate produced from the organic matter contained in the soil fluctuates within very narrow limits and is poorly suited to show the vast differences in nitrifying powers that must exist between these soils so diversely treated. There is a very close parallelism between the data representing the

other three methods employed. Especially is this true when ammonium sulfate and ammonium sulfate and lime are compared. The same comparative relationship exists, even though much more nitrate is produced in the presence of lime. Apparently, the normal buffer capacity of this soil is great enough to maintain its normal equilibrium in the presence of this amount of ammonium sulfate, so as to yield comparative results. In general, the nitrification of blood meal yields results quite comparable with the ammonium sulfate treat-

TABLE 1
Fertilizer treatments and nitrification tests on Willamette silty clay loam
(Parts per million nitrogen as nitrate)

PLOT NO.	FERTILIZER TREATMENT	100 GM. OF SOIL	30 MG.M. OF N AS (NH ₄) ₂ SO ₄ PER 100 GM. SOIL	30 MG.M. OF N AS (NH ₄) ₂ SO ₄ + 210 MG.M. CaCO ₃ PER 100 GM. SOIL	0.1 PER CENT N AS BLOOD MEAL PER 100 GM. SOIL
13	No fertilizer	6.0	19.8	127.0	128.5
14	100 pounds nitrate plus 60 pounds blood meal	5.38	19.9	103.5	111.5
15	160 pounds potassium sulfate	5.20	31.1	131.5	139.2
16	320 pounds superphosphate	5.33	29.4	129.9	148.2
17	No fertilizer	5.80	32.7	162.7	160.3
18	3000 pounds hydrated lime	6.94	132.9	328.5	355.0
19	320 pounds flowers of sulfur	5.51	18.7	86.5	122.2
20	Manure (12 tons per acre)	6.26	37.1	161.5	192.2
21	No fertilizer	5.10	36.5	147.1	198.1
22	100 pounds nitrate, plus 60 pounds blood meal, plus 160 pounds potassium sulfate, plus 320 pounds superphosphate	5.38	31.1	142.8	151.6
23	160 pounds potassium sulfate plus 320 pounds superphosphate	5.14	26.1	130.1	144.7
24	320 pounds sulfur, plus 320 pounds superphosphate, plus 160 pounds potassium sulfate	5.70	16.0	92.6	169.7
25	No fertilizer	6.17	30.7	140.7	134.0
B-15	6 tons limestone per acre (fallow plot)	5.42	133.0	254.4	325.0
C-15	4 tons limestone per acre (fallow plot)	5.20	29.5	166.9	222.2
D-15	2 tons limestone per acre (fallow plot)	5.76	19.0	134.6	173.1
E-15	No fertilizer (fallow plot)	5.12	24.7	116.7	150.5

ments, the only outstanding contradiction being in plot 24 which had been heavily treated with sulfur, superphosphate, and potassium sulfate.

It would be only natural to expect that an organic nitrogenous substance would be better adapted to this soil. Whether a similar picture could be obtained by using soils containing smaller amounts of buffer is only conjecture, but for the conditions of this experiment it is apparent that ammonium sulfate plus an equivalent of calcium carbonate, and 0.1 per cent of blood meal should

both be used in a comparison of the nitrifying powers of a series of fertilizer plots.

The relationship of the nitrifying power of the soil as determined in the laboratory to the actual amount of nitrate produced under field conditions can

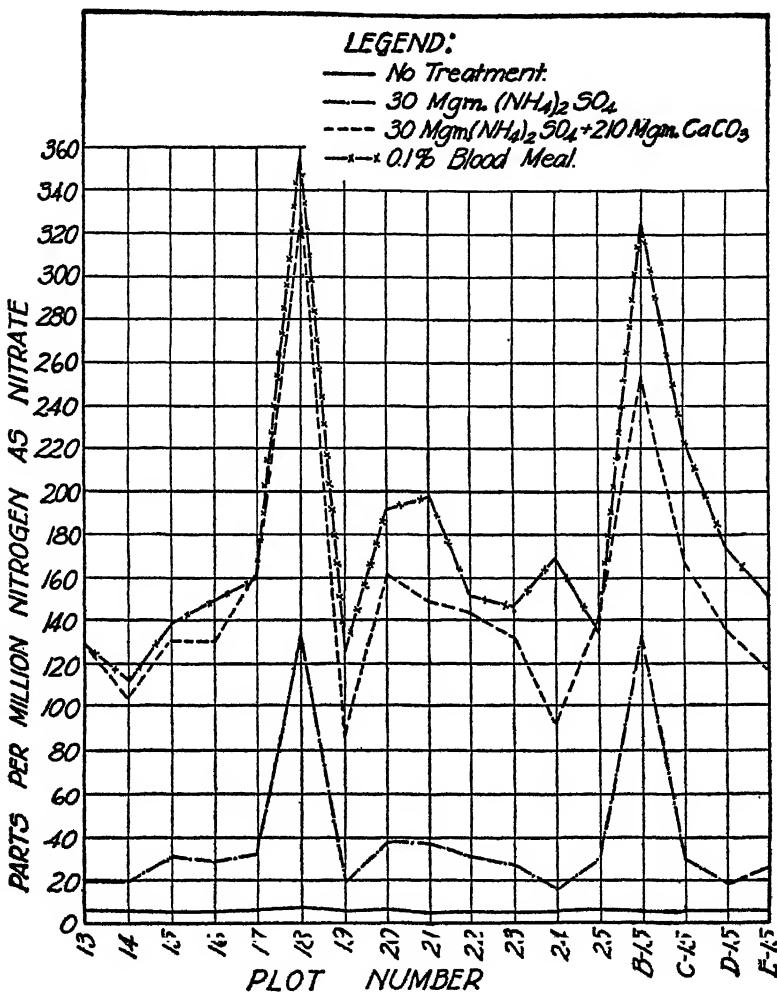


FIG. 1. RESULTS OF NITRIFICATION TESTS

seldom be established unless fallow plots are available. In a previous article (2) the author has reported the nitrate content of the fallow plots receiving no lime, 2, 4, and 6 tons of lime per acre (listed at the bottom of table 1) during the growing season. A study of these data shows that the nitrate content was greatest where the most lime was applied, which is in direct agreement with

TABLE
Fertilizer treatments and nitrification tests on *Umatilla* medium sand
(Parts per million nitrogen as nitrates)

PLOT	FERTILIZER TREATMENT	2 WEEKS' INCUBATION				3 WEEKS' INCUBATION				4 WEEKS' INCUBATION			
		100 gm. soil	100 gm. soil plus (NH ₄) ₂ SO ₄	100 gm. soil plus K ₂ SO ₄	100 gm. soil plus CaSO ₄	100 gm. soil	100 gm. soil plus (NH ₄) ₂ SO ₄	100 gm. soil plus K ₂ SO ₄	100 gm. soil plus CaSO ₄	100 gm. soil	100 gm. soil plus (NH ₄) ₂ SO ₄	100 gm. soil plus K ₂ SO ₄	100 gm. soil plus CaSO ₄
1	100 pounds NaNO ₃	10.5	74.1	108.0	67.8	12.4	83.3	78.5	13.4	67.7	400.0	102.8
2	100 pounds NaNO ₃ plus 160 pounds K ₂ SO ₄	10.1	39.6	129.0	78.4	9.2	31.2	205.0	79.1	14.2	69.0	296.0	85.0
3	No fertilizer	10.6	44.0	268.0	70.0	16.1	59.7	235.0	74.0	14.0	45.0	284.0	90.0
4	160 pounds KCl	18.0	42.5	115.0	81.5	15.5	33.3	200.0	75.4	13.4	31.3	250.0	94.6
5	320 pounds P ₂ O ₅	15.8	35.5	200.0	82.5	11.1	43.0	222.0	83.3	18.7	47.0	320.0	82.6
6	320 pounds P ₂ O ₅ plus 160 pounds KCl	23.9	25.6	136.0	76.5	19.2	62.5	210.0	89.0	15.0	30.0	217.3	77.7
7	No fertilizer	12.6	42.7	169.0	72.5	10.5	69.0	222.0	100.0	19.8	24.0	302.0	84.1
8	200 pounds CaSO ₄	11.9	53.4	174.0	103.0	13.35	56.4	200.0	83.3	16.7	47.6	225.8	108.0
9	No fertilizer	13.7	68.5	261.0	88.0	16.2	45.0	183.0	78.4	15.9	45.0	87.4
10	200 pounds sulfur	17.2	94.1	190.1	74.0	9.65	39.6	160.0	93.0	22.0	57.5	82.6
11	No fertilizer	8.97	48.0	189.0	78.2	12.2	35.7	200.0	95.2	13.7	39.6	83.4
12	200 pounds NaNO ₃ plus 160 pounds P ₂ O ₅	8.8	47.5	164.5	72.0	8.9	56.4	210.0	74.0	22.0	36.0	235.0	83.1
13	350 pounds N P K	17.5	57.5	189.5	81.5	12.7	52.6	154.0	80.0	18.2	28.0	222.0	78.5
14	No fertilizer	15.6	32.5	178.0	64.0	8.85	50.5	222.0	70.0	18.4	54.9	222.0	72.1

the nitrifying powers as determined in the laboratory. These data are of more significance in view of the fact that these plots were relatively unproductive, having been cropped continuously to cereals and having received no fertilizer or manurial treatment until the lime was applied. The correlation between the amount of nitrate accumulating under field conditions and the relative nitrifying powers of these plots, as determined by the several methods employed, establish the validity of these methods when used on soil of this type.

Umatilla medium sand represents widely contrasting conditions to the Willamette silty clay loam. The fact that this soil comes from a semi-arid region where about four and one-half feet of irrigation water is used annually indicates the lack of organic matter and the extreme porosity of the soil. This soil does, however, produce good crops of alfalfa and cereals. Table 2 shows the fertilizer treatments and nitrifying powers of the various plots under observations.

The 4-weeks incubation studies were made first, but, because of lack of correlation of results and the extreme oxidation of the ammonium sulfate added in the presence of lime, it was thought that, on light sandy soils of this type representing extreme aeration and lack of buffer capacity, a shorter incubation period might show consistent variations in the ability of the nitrifying flora of the plots variously treated so as to present a picture comparable to table 1. Hence the test was repeated using 2- and 3-weeks incubation periods.

In comparing the data obtained from the different incubation periods, we find that the nitrification of the soil's own nitrogen is generally higher than on the heavy soils, at times representing more than three times as much nitrogenous material oxidized, though this soil is definitely low in organic matter, and further that the amount fluctuates between the various incubation periods so as to represent wide variations. This would lead to the opinion that, even in soils of low organic content, the nitrate content is relatively unstable and varies as species relationships of the various biological forms present fluctuate.

In comparing the data from the columns representing the nitrification of ammonium sulfate, we find that generally the maximum nitrate accumulation is found during the third week and that following this period radical fluctuations in the amount of nitrate may be observed. Obviously the period of incubation in the presence of this amendment must not be more than 3 weeks, and, since the nitrate production in 2 weeks is nearly equal to that of the 3-week period, the shorter period would be most desirable.

When a comparison is made of the columns representing nitrification of ammonium sulfate in the presence of an equivalent of lime, we find that nitrification progresses more rapidly in the presence of the lime, that the maximum amount was found in the 4-week period, and that this amount was progressively greater than in the shorter incubation periods. For this test, the best incubation period is not so clearly defined; either period would probably be equally satisfactory.

TABLE 3
Relation of length of incubation period to nitrifying power using different amounts of $(NH_4)_2SO_4$

			1 WEEK			2 WEEKS			3 WEEKS			4 WEEKS		
			Ammonium sulfate			Ammonium sulfate			Ammonium sulfate			Ammonium sulfate		
			N	N	N	N	N	N	N	N	N	N	N	N
<i>Soil I</i> —(loam) pH 7.76	mgm. N as NO_3^-	2.64	3.5	4.5	4.0	2.63	6.4	6.84	4.22	3.77	14.81	9.80	6.04	3.66
	Percent nitrified*.....		2.86	18.6	54.4	12.56	42.1	63.6	36.8	60.3	91.0	50.3	50.3	18.75
<i>Soil II</i> —(sandy loam) pH 7.28	mgm. N as NO_3^-	1.01	1.61	2.21	1.77	0.98	3.87	3.03	1.90	2.27	4.95	4.61	3.63	1.52
	Per cent nitrified*.....		2.0	12.0	30.4	9.63	20.5	37.0	8.93	23.4	54.4	17.13	41.4	5.66
<i>Soil III</i> —(no fertilizer clay loam) pH 6.32	mgm. N as NO_3^-	0.56	1.34	1.7	1.84	0.84	2.11	3.42	2.09	1.14	4.70	4.66	2.98	1.46
	Per cent nitrified*.....		2.6	11.4	43.4	4.23	25.8	50.0	11.86	15.2	73.6	14.73	41.7	5.88
<i>Soil IV</i> —(sulfured silty clay loam) pH 5.93	mgm. N as NO_3^-	2.2	3.1		1.88	2.87	3.57	3.06	1.09	3.83	4.61	2.82	1.90	5.15
	Per cent nitrified*.....		3.0		3.3	16.9	47.2	9.13	35.2	69.2	10.73	37.6	85.6	5.66

* Calculated after subtracting check from total nitrates formed.

When 0.1 per cent of blood meal is used as a source of nitrogen, 2 weeks incubation yields almost as large quantities of nitrates as the longer periods and it is possible that even a shorter period would have been more desirable.

In comparing the amount of nitrate produced in these soils at the end of each incubation period we find little correlation between the several methods employed. Nitrification takes place rapidly but the buffer capacity is so limited that the ordinary amounts of nitrogenous materials used for determining the nitrifying powers of soils exert a maximum chemical effect which masks the variations in the nitrifying powers that must exist between plots receiving such widely varying fertilizer treatments. Apparently smaller quantities of nitrogenous materials should be used in nitrification tests in this soil and correspondingly shorter incubation periods should be employed.

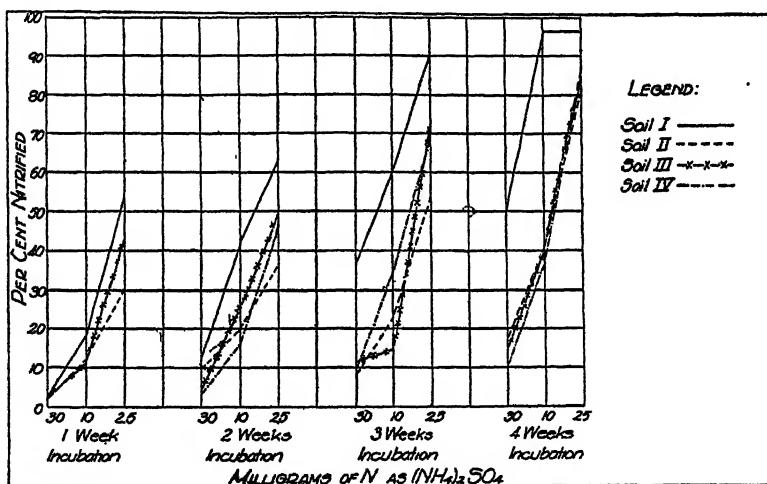


FIG. 2. RELATION OF INCUBATION PERIOD TO NITRIFYING POWERS WHEN DIFFERENT AMOUNTS OF $(\text{NH}_4)_2\text{SO}_4$ ARE USED

One factor which may nullify the residual effects of the fertilizers applied in the field is that these soils receive about four and one-half feet of irrigation water annually. Considering the extreme oxidation of organic matter which takes place and the washing which is brought about by the irrigation water there may not be much residual effect produced by the fertilizer treatment. Crop yields on these plots also fail to show consistent benefit from the use of the various fertilizers applied. Since the amounts of nitrates produced in these tests fluctuate widely, however, and show differences just as great as in normal soils yet lack significance because of inconsistency, we are forced to conclude that, unless better correlation can be obtained by further varying the conditions of the test by using smaller quantities of nitrogenous materials

and shortening the incubation period, they are of little value under these extreme conditions.

To check further on the relation of the amount of ammonium sulfate used in determining the nitrifying power, to the period of incubation and the physical and chemical condition of the soil, four productive soils of the Willamette Valley were used. Soils I and II are known as "river bottom" soils and are classified as loam and sandy loam, respectively. These soils are occasionally flooded by the Willamette River. Soils III and IV are silty clay loam and came from the fertilizer plots described in table 1.

These soils were treated with varying amounts of nitrogen as ammonium sulfate and were analyzed for nitrates at the end of 1, 2, 3, and 4 weeks. The analyses are recorded in table 3 and the percentage of nitrogen oxidized is shown graphically in figure 2.

Examination of these data shows little difference between the nitrifying powers of soils II, III, and IV as indicated by the amount of nitrate produced after each incubation period with the varying amounts of ammonium sulfate added.

Soil I, having a higher nitrifying power, continued to yield more nitrates as the incubation period was lengthened until practically all of the ammonium sulfate had been nitrified in the smaller applications.

When we consider the relation of the period of incubation to the amount of nitrogen added as ammonium sulfate, it becomes apparent that three to four weeks incubation is suitable where 30 mgm. of nitrogen is added, and that two to three weeks are well suited to show the differences where 10 mgm. or 2.5 mgm. of nitrogen is used. One week's incubation was apparently sufficient where 2.5 mgm. nitrogen was used. Though a greater percentage of the nitrogen added is nitrified in a given length of time where smaller amounts are used, the same general relationship exists, which would lead to the assumption that the buffer capacity of these soils is adequate to take care of the acidity formed from the ammonium sulfate.

Another point of interest is that the application of 320 pounds of sulfur per acre showed no effect on the nitrifying power of the heavy soil in the presence of 30 mgm. of nitrogen as ammonium sulfate. So we must conclude that the normal buffer capacity of these heavy soils must be great enough to take care of more acidity than is produced from 30 mgm. of nitrogen when applied as ammonium sulfate.

The above data restore confidence in the use of ammonium sulfate as a source of nitrogen for nitrification tests when used on normally productive soils.

SUMMARY

In reviewing the data presented, it is apparent that, on heavy, well-buffered soils, by using the usual 4 weeks' incubation period, a consistent parallelism of variations in the nitrifying powers of fertilizer plots may be

obtained by the several modifications of the soils method for determining the nitrifying powers of these soils.

Extremely sandy soils of low buffer capacity and low organic content do not yield consistent results when the same amounts and kind of nitrogenous materials are used. Judging by the data presented, not more than 2 weeks' incubation should be used, and smaller amounts of nitrogenous materials must be added. It must be remembered that this represents the extreme in agricultural soils. It is an arid sand of no agricultural value except where sufficient irrigation water is available.

Normally productive soils studied representing sandy loam, loam, and clay loam types possess enough buffer capacity to take care of the amount of acidity produced from 30 mgm. of nitrogen as ammonium sulfate in a 28-day incubation period. Where smaller quantities are used a shorter incubation period is necessary. Two weeks' incubation is well suited to an application of 2.5 mgm. nitrogen as ammonium sulfate and 3 weeks to a 10 mgm. application.

The data submitted here sustain the validity of the use of ammonium sulfate as a source of nitrogen for nitrification tests on normally productive soils.

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THE HYDROMETER METHOD FOR MAKING A VERY DETAILED MECHANICAL ANALYSIS OF SOILS

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In a recent communication (2) it was shown that the hydrometer method can be used for determining the combined sands, silt, and clay or colloids in only 15 minutes. For general purposes these three main divisions are sufficient. In many detailed soil studies, however, a greater number of textural divisions is necessary and advisable.

It has been found that by applying Stokes' law to the data obtained by the hydrometer method, a soil can be divided into any desired number of textural divisions. Although there may be many objections to the employment of Stokes' law in making a mechanical analysis of soils, yet it gives many fundamental comparisons of soils, and therefore has been adopted by the International Soil Congress (3) as an aid to the mechanical analysis of soils.

By the combination of Stoke's law and the hydrometer method, it is now possible to determine simply, quickly, and extensively the range of size and the amount of soil material that falls within this range, and thus any number of textural divisions can be made.

METHOD

The method of making a mechanical analysis of soils by the combination of Stokes' law and the hydrometer method consists first of ascertaining the size of particles that fall at various times under the procedure used in the hydrometer method and than taking readings on the hydrometer at those periods.

The formula used in calculating the size of particles at the various rates of falling is shown below. The height of column and the temperature used in the calculations were $32\frac{1}{2}$ cm. and 20°C . respectively. The height is measured from the top of the soil suspension column with the hydrometer in it to the point where the solid soil column is being formed.

$$v = \frac{2 g d^2 (S - S_1) \cdot 6}{9 \pi t \cdot 40}$$

v = Distance one particle of d size falls in 1 minute.

g = Pull of gravity (980).

d = Diameter of particle (mm.).

S = Specific gravity of soil (2.65).

S_1 = Specific gravity of water (1).

n_t = Coefficient of viscosity of water.

$\frac{6}{40}$ = Used to express v in terms of cm. per minute and also diameters in mm.

According to this formula the sizes of particles that will fall at the various times in a column $32\frac{1}{2}$ cm. high and at a temperature of 20°C . are:

Time of sedimentation	Diameter of particles mm.	Time of sedimentation	Diameter of particles mm.
1 minute	0.077846	12 hours	0.0029
2 minutes	0.055050	13 hours	0.00279
5 minutes	0.034814	14 hours	0.00270
15 minutes	0.02010	15 hours	0.00259
30 minutes	0.014212	16 hours	0.0025
60 minutes	0.01005	17 hours	0.00243
2 hours	0.0071	18 hours	0.002369
3 hours	0.0056	19 hours	0.002307
4 hours	0.00502	20 hours	0.00223
5 hours	0.0045	21 hours	0.00219
6 hours	0.0041	22 hours	0.00214
7 hours	0.0038	23 hours	0.00209
8 hours	0.00355	24 hours	0.00205
9 hours	0.00335	48 hours	0.00145
10 hours	0.00318	96 hours	0.001025
11 hours	0.00303		

The foregoing figures for size of particles signify the upper limit of size of any particle that stays in suspension at any given time. For instance, at the end of 1 minute the upper limit of any particle that may still stay in suspension is 0.077846 mm. in diameter, at the end of 1 hour 0.01005 mm., etc.

If one takes hydrometer readings at all the various periods shown above, one will have a very complete picture of the size and amounts of the various particles, or a complete distribution curve, in any one soil. It is probably not important, however to take all the above readings. It has been decided that the most important readings are those taken at the end of 1, 2, and 15 minutes and at the end of 1, 4, 8, and 24 hours. These periods would give particles 0.077846, 0.055050, 0.02010, 0.01005, 0.00502, 0.00355, and 0.00205 mm. respectively. This would afford four divisions for silt; namely, 0.055050, 0.02010, 0.01005, and 0.00502 mm., and three divisions for clay or colloids; namely, 0.00502, 0.00355 and 0.00205 mm. Hence, both the silt and clay are divided into a greater number of division in the hydrometer method than in the regular mechanical analysis.

Unfortunately it is not possible to subdivide the sands by the hydrometer method as it is the silt and clay or colloids. For subdividing the sands, the soil suspension, after it has been used for all the necessary hydrometer read-

ings, is poured into a 150-mesh sieve and water run over it from the faucet to wash away all the material that will go through the sieve. The sieve will retain all the coarse material up to and including fine sand. The sands retained in the sieve are then dried and passed through the different size sieves to determine the amounts of the various size sands. The very fine sand is determined by difference, for the total amount of sand is known quite accurately from the hydrometer reading at the end of 1 minute (3).

Although the separation of the various sands by the above procedure may not be accurate, yet it is approximately correct. The total amount of sand, however, as revealed by the hydrometer reading, is quite correct.

Temperature affects the hydrometer readings by affecting both the density of water and the rate of settling of the soil particles. Since the soil suspensions have to stand for many hours, it is necessary that the temperature should stay constant during this period. Various devices can be used to maintain a fairly constant temperature. It has been found, however, that the most practical method is running tap water. Any kind of a container that will hold the cylinders can be arranged so that the tap water enters and runs off thus maintaining a constant temperature. At this laboratory the temperature of the tap water was about 13°C. and varied little, if any, during the 24-hour period. Indeed the arrangement worked remarkably satisfactorily.

The procedure followed in making hydrometer readings in this constant temperature bath was as follows: The soil suspensions were prepared exactly according to the methods described previously (1), then the cylinder containing the soil suspension and the hydrometer was placed in the constant temperature bath and allowed to stand there with occasional stirring with a rod, until the contents attained the temperature of the bath. The cylinder then was taken out and the contents were shaken vigorously. The cylinder was placed on the table and the time was noted quickly. The hydrometer was then placed in the cylinder and at the end of 1 and 2 minutes the hydrometer readings were taken. It will be noted that during the first 2 minutes the cylinder was not in the constant temperature bath but in room temperature. The first two readings were taken out of the constant temperature bath because of the difficulty in placing the cylinder into the bath quickly enough after shaking it to take a correct reading at the end of 1 minute. The error that may arise from any change in temperature is slight and corrections can be made for it. After the reading was taken at the end of 1 or 2 minutes the cylinders were returned to the temperature bath and the readings taken at the stated intervals. Before the reading was taken the hydrometer was pushed down gently to avoid any lagging. All the hydrometer readings then were reduced to 67°C. as described previously (1).

For the heavier types of soil 50 gm. should be used, but for the sands and light sandy loams 100 gm. should be employed.

As stated in previous papers, the hydrometer was calibrated against actual soil suspensions. Its readings, therefore, are quite accurate. It was found

very difficult to calibrate the range from 0 to 10 gm. per liter, however, and this range is not so accurate as the rest of the range. But if 100 gm. is employed the error is very small.

The number of soils whose detailed mechanical analysis can be examined by the hydrometer method as described above, is limited mainly by the number of hydrometers and the number of cylinders that one cares to invest in. When it is considered that hydrometer readings are taken only at the end of 1, 2, and 15 minutes, and 1, 4, 8, and 24 hours, it is readily realized that a large number of soils can be started and run at the same time. It is very easy and practical to examine ten soils in about 25 hours by using ten hydrometers and ten cylinders. This is a great contrast to the time required to make a mechanical analysis of a single soil: And the important thing is that the mechanical analysis will not subdivide the soil particles into as many classes as the hydrometer method does.

EXPERIMENTAL DATA

In table 1 is shown the detailed mechanical analysis of a number of representative types of soils, as obtained by the hydrometer method with the aid of Stokes' law. This mechanical analysis represents a more detailed subdivision of the silt and clay or colloid fractions of the soil. The subdivisions of the sand fraction are not shown in this table because, as discussed previously, they are obtained by the sieve method. However, the total amount of sand in each soil is shown in table 1 by difference, as for instance, all the soil material that is not in suspension at the end of 1 minute is sand (2).

According to Stokes' law the dividing point between very fine sand and silt would be at the end of 2 minutes, but according to the comparison of the hydrometer method and the mechanical analysis as shown previously (2) the dividing point would be at the end of 1 minute. In table 1, the results for both periods are shown. Since the actual mechanical analysis of 30 different soils, as obtained by the U. S. Bureau of Soils, shows that the percentage of the material that settles out at the end of 1 minute in the hydrometer method (2) is equal to the percentage of all the combined sands as obtained by the mechanical analysis, the data at the end of 1 minute may be taken as the dividing point between the sand and silt. Since this dividing point disagrees slightly with that of Stokes' law it may appear that the error is considerable. It is believed, however, that the actual error is probably very small because of compensating factors.

The data in table 1 show many most interesting and important facts. In the first place they show that the hydrometer method with the aid of Stokes' law can be employed very successfully to determine the amount and size of the various soil particles in soils, and consequently to obtain simply and quickly a very detailed mechanical analysis of soils. It will be seen that there are six divisions in the silt and clay or colloid fractions. In the second place, they reveal the fact that the proportion of the different soil particles varies tremendously in

the diverse soils with great extremes. For instance, soil 3 had practically only two groups or sizes of particles, sand and clay or colloids, because the material that stayed in suspension was practically the same for all the different periods. Indeed, after the 15-minute period of standing and for the next 24 hours there was hardly any change in the material staying in suspension. As will be noted, the amount of material staying in suspension at the end of 1 minute is 35 per cent, at the end of 15 minutes 30 per cent, and at the end of 24 hours, 28.6 per cent, or a difference of only 1.4 per cent between the 15 minutes and the 24 hours.

On the other hand as a contrast to soil 3, soil 5 has a great range of size of soil particles, because the soil particles continued to fall and settle very regularly and rapidly with the time of standing. At the end of 1 minute, for instance,

TABLE 1

Percentage of soil material still in suspension whose upper limit of size is indicated at each period

TIME.....	1 minute	2 minutes	15 hours	1 hour	4 hours	8 hours	24 hours
DIAMETER.....	0.077846 mm.	0.05505 mm.	0.02010 mm.	0.01005 mm.	0.0050 mm.	0.0035 mm.	0.00205 mm.
	per cent	per cent	per cent	per cent	per cent	per cent	per cent
Soil 1	76.0	72.0	63.0	53.0	42.0	36.0	28.0
2	52.0	47.0	42.2	40.0	36.6	36.4	33.0
3	35.0	33.4	30.0	24.0	29.0	28.6	28.6
4	38.0	35.0	31.5	21.0	22.0	19.0	14.5
5	60.0	54.2	29.0	20.0	12.0	8.6	4.6
6	48.0	43.5	36.1	15.5	10.0	7.10	4.3
7	35.0	29.0	20.0	15.0	9.0	6.00	4.0
8	43.0	36.0	25.0	17.0	11.0	6.60	3.4
9	15.0	13.8	10.1	6.5	4.0	3.50	2.1
10	38.5	34.6	21.1	12.1	5.5	3.50	1.2
11	8.5	7.2	5.5	4.1	2.5	2.10	1.0
12	21.5	18.2	10.7	6.0	2.1	1.3	0.3
13	18.1	15.1	9.0	4.8	1.8	1.0	0.2
14	1.8	1.1	0.8	0.8	0.7	0.7	0.5

there was 60 per cent of the material still in suspension, at the end of 15 minutes 29.0 per cent, and at the end of 24 hours only 4.6 per cent. Apparently this soil is fairly equally distributed in all the various sizes.

Soil 14 is somewhat like soil 3 with the exception that the former is composed almost entirely of sand which settles out at the end of 1 minute and there is very little material that settles out after that.

These three soils represent the extremes of the soils contained in the table. The other soils show all variations between these extremes.

The amount of material between any two ranges of size of soil particles can be determined by difference and thus both the range of size and the amount in that range, are known.

All the 14 soils listed in table 1 can be examined and the detailed mechanical

analysis shown can be obtained in only 1 or 2 days, whereas the regular mechanical analysis would take many weeks to accomplish with more work and with less detailed results.

In previous communications the hydrometer method was proposed for determining the colloidal content of soils and also for dividing the soil material into three main groups, sand, silt, and clay or colloids in only 15 minutes. In the present paper much longer periods are employed for determining the finer material of the soil. As a consequence, it may appear that there is inconsistency in these various proposals.

A critical examination, however, shows that these various proposals are not inconsistent, but that each has been offered to serve a specific purpose. For instance, the 15-minute period is employed for making a broad and general division between the colloidal and non-colloidal material in the soil; in other words, the 15-minute period seems to mark the transitional point between the colloidal and the non-colloidal material. Now the colloidal material may vary tremendously in size of particles, and it can be subdivided into any number of classes, and to each class or division any name may be given that one desires. In the present paper an attempt has been made to divide the colloidal portion of the soil into a larger number of divisions than in the previous work and this work is in no way contradictory to, but simply an elaboration of the previous work.

In comparing the claim that the hydrometer method can determine the total colloidal content of soils in only 15 minutes with the figures of the upper size limit of particles in Stokes law, it must be remembered that there are certain compensating factors in the hydrometer method which tend to give the true final result (1) and which the mathematical calculations do not take into account.

SUMMARY

With the aid of Stokes' law the hydrometer method can be used to make a very detailed mechanical analysis simply and quickly. More than ten soils can be analysed in one or two days and a greater number of textural divisions can be obtained than in the regular mechanical analysis method.

The method appears to be sound and to have great promise.

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CONTRIBUTION TO THE CHEMICAL COMPOSITION OF PEAT:

II. CHEMICAL COMPOSITION OF VARIOUS PEAT PROFILES

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It has been shown in the previous contribution (6) that peats of different origin can be subjected to a careful chemical analysis, which allows us to determine the exact chemical nature of the various constituents of the peat. Instead of assuming the existence of various humic acids, a group of heterogeneous substances which are extracted from peat by alkalies and the chemical nature of which remains unknown up to the present time, we can divide the organic complexes of peat into a number of definite chemical groups which correspond to the types of constituents present in natural plant materials. This system of analysis enables us to differentiate between different peat formations; it contributes to our understanding of the degree of decomposition that the peat-forming plants have undergone; and it throws definite light upon the processes that have taken place in the formation of peat from the plant remains.

In the analysis of different peat profiles it is first of all important to establish whether the various horizons which have been formed at different times, frequently from different plants and under varying conditions, show marked variations in their chemical composition. Attention may be called here to the fact that the chemical composition of a definite peat layer or of a certain peat formation depends primarily upon three factors: 1. The nature of the plant remains which have contributed to the formation of the particular peat layer; 2. The environmental conditions predominating during the time of the formation of the particular layer and soon after—aeration, moisture, supply of nutrients, and reaction are to be considered as the most important factors in this connection; 3. Nature and extent of the processes of decomposition of the plant residues by microorganisms.

The peat materials used in these investigations were selected primarily with the idea of obtaining further information in regard to the application of the methods previously outlined to the study of the chemical nature of peat as well as in connection with the problem of the origin of peat.¹

¹ Some of the peat profiles were carefully taken in a fresh condition in New Jersey by the authors. Other profiles as well as certain samples of peat were obtained from Dr. A. P. Dachnowski-Stokes of the Bureau of Chemistry and Soils, United States Department of Agriculture, to whom acknowledgment is hereby made. The authors are also indebted to the Hyper-Humus Company of Newton, N. J. for the assistance rendered in connection with the sampling of profile A.

These peat materials can be described as follows:

A. *Lowmoor peat* of Newton, N. J. This represents a typical lowmoor peat with a predominant *Carex* vegetation on the surface. The samples were taken from a part of the bog which is still in a natural, undrained and uncultivated condition. Three samples ($A_1 - A_3$) were taken from one profile, and three ($A_4 - A_6$) from the lower part of another profile not far distant.

A_1 was taken just below the surface vegetation to a depth of 12 cm., in close proximity to the roots and rhizomes of the living *Carex* plants.

A_2 , from the same profile, at a depth of 80 cm. and consisting largely of *Phragmites* peat.

A_3 , from same profile, at a depth of 160 to 180 cm. largely woody in nature, with an admixture of *Phragmites*, ferns, and pollen.

A_4 , at a depth of 160 cm., representing a layer of forest material and *Phragmites* from the other profile.

A_5 , at a depth of 180 to 200 cm., lake peat layer, equivalent to Lebertorf.

A_6 , the mud or Gyttja layer, rich in diatoms, shells of mollusks, just above the underlying marl layer.

A_7 , represents a mixture of pieces of wood selected from layers A_3 and A_4 ; the adhering peat has been washed off, and the wood was dried and ground for analysis.

B. *Mixed forest-Carex peat*, with considerable sphagnum beginning to develop in patches on the surface, taken from a cranberry bog, at Whitesbog, N. J. Only one sample was analyzed, namely B_1 , representing the layer just below the surface vegetation.

C. *Forest peat*, taken from a so-called juniper swamp in Queens, New York. C_1 is a sample of typical forest peat, at a depth of 30 cm. C_2 is a thin layer of *Sphagnum cuspidatum* peat, about 3 cm. thick, surrounded by the forest peat, found at a depth of 25 to 30 cm.

D. *Saw grass (Cladium) peat*, from the Everglades, Florida.

D_1 represents a portion of *Cladium* peat taken from the surface 20 cm. of a drained and cultivated portion of the bog.

D_2 represents a fresh sample of *Cladium* peat from a part of the natural undrained peat area at Okeelanta, Fla.; well defined, brown fibrous *Cladium* about 15 to 20 cm. thick and about 1 meter below the surface.

Analysis of this sample has previously appeared in a paper by Dachnowski (2).

E. *Highmoor peat from Oldenburg, Germany*, taken and brought to this country by Dachnowski-Stokes,² for the peat exhibit of the first International Congress of Soil Science. Samples E_1-E_{11} represent the two main divisions described by Dachnowski (1) as "sphagnum," "heath" and forest peat.

E_1 represents the upper 15 to 16 cm. of the profile (in a dry condition), light brown in color, fibrous (largely *Sphagnum medium*, *S. fuscum*, *S. teres* mixed with some *Calluna* and certain *Ericaceae*).

E_2 , 17 to 22 cm. deep, dark brown, much more compact than E_1 (*S. imbricatum*, *S. papillosum*, *Amblystegium stramineum*).

E_3 , 22 to 40 cm. deep, light brown (largely *S. fuscum* mixed with *Calluna*).

E_4 , 40 to 60 cm., brown, somewhat more compact stratum, similar to E_3 .

E_5 , 60 to 90 cm., fibrous sphagnum layer mixed with some *Calluna* and tufts of *Eriophorum vaginatum*.

E_6 , 90 to 100 cm., dark brown, compact sheath-shrub peat (Grenzhorizont).

E_7 , layer below the Grenzhorizont, older sphagnum peat very compact, dark brown.

E_8 , continuation of E_7 .

² Otherwise Dachnowski.

E₉, lower layer of old sphagnum peat.E₁₀, older sphagnum peat with seam of hypnum peat.

TABLE 1
Reaction, moisture, ash, and nitrogen content of different types of peat

NUMBER OF SAMPLE	TYPE OF PEAT	DEPTH	ORIGINAL	REACTION	ASH	NITROGEN
			MOISTURE			
A ₁	Lowmoor (Newton)	12	78.7	5.9	13.22	3.734
A ₂	Lowmoor (Newton)	80	86.6	6.3	10.13	3.059
A ₃	Lowmoor (Newton)	160-180	90.5	6.3	10.15	2.438
A ₄	Lowmoor (Newton)	160	86.2	6.7	15.00	3.238
A ₅	Lowmoor (Newton)	Lake peat	88.1	6.8	24.87	3.159
A ₆	Lowmoor (Newton)	Gyttja	80.9	8.0	59.55	1.681
A ₇	Lowmoor (Newton)	Wood	5.3	3.85	0.875
B	Forest (and Carex)	Surface	80.8	3.7	20.85	1.829
C ₁	Forest	30	4.7	3.30	2.480
C ₂	<i>Sph. cuspidatum</i> (forest)	30	5.30	1.310
D	Lowmoor (Cladium, Everglades)	Drained, upper 20 cm.	6.8	13.38	3.448
D ₂	Lowmoor (Cladium, Everglades)	Undrained, upper layer	6.2	7.3	3.510
E ₁	Highmoor (Germany), younger sphagnum	15	4.11	1.72	0.836
E ₂	Highmoor (Germany), younger sphagnum	17-22	4.3	1.85	0.817
E ₃	Highmoor (Germany), younger sphagnum	22-40	1.50	1.053
E ₄	Highmoor (Germany), younger sphagnum	40-60	2.36	0.977
E ₅	Highmoor (Germany), younger sphagnum	60-90	1.82	0.815
E ₆	Grenzhorizont	90-100	1.71	1.120
E ₇	Older sphagnum	100-120	1.38	0.925
E ₈	Older sphagnum	4.2	1.13	0.992
E ₉	Older sphagnum	4.3	1.16	0.681
E ₁₀	Older sphagnum	4.4	2.22	0.900
E ₁₁	Woody peat, bottom of profile	4.2	5.03	1.453
E ₁₂	Pieces of wood from E ₁₁	4.4	0.81	0.548
F	Scirpus peat	6.1	7.9	1.58
G	Hypnum peat	5.8	36.5	1.43
H	Dopplerite	5.1	2.3	3.06
I	Sedimentary peat	7.2	25.3	3.31

E₁₁, lowest layer of profile, consisting of woody peat, derived from ancient birch-pine forest.E₁₂, pieces of wood selected from the E₁₁ layer.

F. *Tule* (*Scirpus* sp.) peat, from Santa Anna, California.

G. *Hypnum* peat, consisting of *Amblystegium scorpioides* from Wisconsin.

H. Sample of *Dopplerite*, brought by Dachnowski-Stokes from Holland.

I. Sedimentary peat, from Dollar Lake, Michigan.

The reaction, original moisture content (in the fresh samples taken by the writers only), and the ash and nitrogen content of the various peat samples are given in table 1.

None of the samples of the lowmoor peats were very acid, the hydrogen-ion concentration decreasing with depth and the material actually becoming alkaline in the lake peat layer and below. The ash content is relatively high, increasing with depth. The nitrogen content is high. The particles of wood taken from the lower portions of the lowmoor profile contained the smallest amount of ash and nitrogen and had the lowest pH value. The *Cladium*,

TABLE 2

Chemical composition of several horizons of a lowmoor peat profile from Newton, N. J.

(On per cent basis of dry material)

NUMBER OF HORIZON	DEPTH cm.	ETHER-SOLUBLE FRACTION	WATER-SOLUBLE FRACTION	HEMICELLOSE	CELLULOSE	LIGNIN (ASH AND NITROGEN-FREE)	CRUDE PROTEIN	ASH	TOTAL	
									L	C
A ₁	12	0.66	3.08	10.31	0	38.35	22.48	13.22	88.10	
A ₂	18	1.10	1.24	8.95	0	50.33	18.72	10.13	90.47	
A ₃	160-180	0.49	2.31	7.02	0	57.83	14.81	10.15	82.61	
A ₄	160	0.78	1.14	7.51	0	42.10	19.81	15.00	86.34	
A ₅	Lake peat	0.67	0.81	12.14	0	33.25	19.38	24.87	91.12	
A ₆	Gyttja	0.36	1.24	5.92	0	15.62	9.81	59.55	92.50	
A ₇	Woody material (160 cm. depth)	1.54	0.86	8.15	6.12	65.02	5.37	3.85	90.91	

Scirpus and *Hypnum* peats show also a high ash and nitrogen content, and a nearly neutral reaction. It is interesting to note that the lower layer of the Florida peat sample contained less nitrogen and less ash than the upper layers, the upper layer of the drained peat being especially rich in ash, probably because of contamination.

The layers of the highmoor peat were distinctly acid in reaction, namely pH 4.1 to 4.4, when determined by aqueous extraction, corresponding closely to the results reported by others. The ash and nitrogen content were low in all samples. Only the lowest woody layer had a high ash content and a relatively high nitrogen content.

The forest peats (B and C) were also acid in reaction, but they had a higher ash and nitrogen content than the highmoor peats; in this respect, they stand midway between the true lowmoor and highmoor peats.

Tables 2, 3 and 4 give the results of analysis of the lowmoor and highmoor peat profiles and of the several miscellaneous peats. The alcohol-soluble fraction was not included in all of these analyses, and, in some cases, the cold- and hot-water-soluble fractions were not included either; this tends to reduce the sum total of the constituents of most of the materials by 3 to 5 per cent.

The ether-soluble fraction is very low in the case of the lowmoor peats; this is true not only of all the layers of the Newton peat, but also of the samples of peat from the Everglades, as well as of the *Scirpus* and *Hypnum* peats. This fraction seldom exceeds 1 per cent of the total material. On the other hand, the ether-soluble fraction of the sphagnum, or the highmoor peats, is very high; this is true of all the layers of the highmoor peat profile, the

TABLE 3

Chemical composition of several horizons of an highmoor peat profile (Oldenburg, Germany)
(On per cent basis of dry material)

NUMBER OF HORIZON	KIND OF PEAT	ETHER-SOLUBLE FRACTION	ALCOHOL-SOLUBLE FRACTION	HEMICELLULOSE	CELLULOSE	LIGNIN (ASH AND NITROGEN-FREE)	CRUDE PROTEIN	ASH	TOTAL
E ₁	Younger sphagnum	3.08	16.88	19.44	34.04	5.23	1.72	80.39
E ₂	Younger sphagnum	6.12	11.09	13.62	49.56	5.11	1.85	87.35
E ₃	Younger sphagnum	3.96	16.24	19.91	38.26	6.58	1.50	86.45
E ₄	Younger sphagnum	5.02	15.44	16.38	40.72	6.11	2.36	86.03
E ₅	Younger sphagnum	4.99	15.12	17.14	43.82	5.10	1.82	87.99
E ₆	Grenzhorizont	7.60	8.44	9.76	54.38	7.00	1.71	88.89
E ₇	Older sphagnum	5.73	9.08	12.38	52.50	5.78	1.38	86.85
E ₈	Older sphagnum	5.18	3.87	9.48	9.63	53.30	6.20	1.13	88.79
E ₉	Older sphagnum	4.28	3.52	10.86	13.74	45.21	4.26	1.16	83.03
E ₁₀	Older sphagnum	5.17	3.72	10.82	10.42	52.62	5.63	2.22	90.60
E ₁₁	Woody peat	5.69	5.13	4.91	4.08	59.86	9.08	5.03	93.78
E ₁₂	Pure wood	2.27	3.45	5.06	11.33	64.12	3.43	0.81	90.47

ether-soluble fraction reaching in one horizon, namely the Grenzhorizont (so called "heath peat"), 7.6 per cent of the total dry matter. It is interesting to note that, with the exception of the lowest bottom layer, namely the woody peat, this horizon contains material which has undergone the greatest decomposition, as indicated by the lowest hemicellulose and cellulose content and the highest lignin content.

The forest peats and the forest-carex-sphagnum peat seem to contain also a large fraction of ether-soluble substances, although the number of samples analyzed is small and the results are, therefore, not sufficient for any generalization.

The ash and nitrogen contents are low in the highmoor peats and high in the lowmoor peats, facts found by many others. Both the nitrogen and the

ash are, however, largely water-insoluble. Although the nitrogen is recorded as protein, it does not necessarily exist entirely in that form in peat. This can be readily demonstrated by two phenomena: 1. Hydrolysis with acids brings into solution only a part of the nitrogen of the peat, while frequently a very large part remains unacted upon by concentrated acids in the cold or by dilute acids (even 5 to 6 per cent H_2SO_4) boiled for a few hours. This reaction is similar to that of the lignins. 2. With an increase in decomposition of fresh organic matter, there is an increase in the amount of nitrogen not readily acted upon by dilute acids.

The total nitrogen in peat can thus be divided into 3 definite fractions:

1. Soluble in cold and in hot water; this includes ammonia, nitrates, amino

TABLE 4
Chemical composition of lowmoor, forest and various other peat samples
(On per cent basis of dry material)

NUMBER OF PEAT	TYPE OF PEAT	ETHER-SOLUBLE FRACTION	WATER-SOLUBLE FRACTION	ALCOHOL-SOLUBLE FRACTION	HEMICELLOSE	CELLULOSE	LIGNIN (ASH AND NITROGEN-FREE)	CRUDE PROTEIN	ASH	TOTAL
B	Forest-Carex-sphagnum	8.80	4.99	0	45.82	11.43	20.85	91.89
C ₁	Forest peat	3.22	5.44	2.68	60.73	14.30	3.30	89.67
C ₂	<i>Sph. cupidatum</i> layer in forest peat	2.78	15.10	17.94	29.14	8.19	8.30	81.51
D ₁	Florida lowmoor, drained	0.40	4.86	0	50.74	21.55	13.38	90.93
D ₂	Florida lowmoor, fibrous Cladium layer	0.93	0.66	1.54	8.48	5.22	45.58	21.75	7.3	91.46
F	Scirpus peat	1.98	0.50	2.01	13.47	6.41	45.91	9.87	7.9	88.05
G	Hypnum peat	0.49	0.96	1.04	11.16	4.07	27.77	8.75	36.5	90.74
H	Dopplerite	1.47	1.30	4.10	14.65	0	42.59	18.81	2.3	85.22
I	Lake peat	0.67	0.70	2.07	14.93	0	23.67	20.69	25.3	88.25

acids, and soluble proteins and is the smallest fraction in peat, whereas in fresh plant materials, especially at an early stage of growth, a third or even more of the nitrogen is in this form. 2. Nitrogen hydrolyzed readily by dilute acids, including boiling for 5 hours with 2 per cent HCl , treatment in the cold with 80 per cent H_2SO_4 , the autoclaving at 120°C. with 5.4 per cent H_2SO_4 ; this fraction can be considered as the true protein nitrogen. 3. Nitrogen not readily acted upon by the above acid treatment.

A series of results on the nitrogen distribution in peat, as shown by the above three fractions, is given in table 6. Because the acid treatment would have to be much more severe to hydrolyze all the protein, no general conclusions can be drawn at the present time. Further data on this subject will be presented later. Attention may only be called to the fact that Jodidi (3)

extracted peat with 63 volumes of 47.5 per cent sulfuric acid, for 28 to 72 hours, at boiling temperature and could bring into solution only 60 to 64 per cent of the nitrogen. Similar results have been obtained by other investigators; in other words, peat contains 30 or more per cent of its nitrogen in a very resistant form. This may be referred to as "humin" nitrogen, not

TABLE 5
Relative total hemicellulose and pentosan content of peat

NUMBER OF PEAT	KIND OF PEAT	DEPTH	HEMICELLULOSE	PENTOSAN
		cm.	per cent	per cent
A ₁	Lowmoor peat	12	10.31	4.72
A ₂	Lowmoor peat	80	8.95	3.66
A ₃	Lowmoor peat	160	7.02	3.50
B	Forest-carex-sphagnum peat	4.99	1.07
C ₁	Forest peat	5.44	0.75
E ₁	Highmoor	15	16.88	7.52
E ₂	Highmoor	17-22	11.09	4.17

TABLE 6
Nitrogen distribution in different peats
(On per cent basis of total nitrogen in peat)

NATURE OF PEAT	SOLUBLE IN COLD AND HOT WATER	HYDROLYZABLE BY DILUTE ACIDS	NON-HYDROLYZABLE BY DILUTE ACIDS
Lowmoor (Newton), A ₁	4.56	58.98	36.46
Lowmoor (Newton), A ₂	2.29	44.15	53.56
Lowmoor (Newton), A ₃	2.27	34.33	63.40
Highmoor (Oldenburg) E ₁	47.86	52.14
Highmoor (Oldenburg) E ₂	16.83	83.17
Highmoor (Oldenburg) E ₃	36.41	63.59
Highmoor E ₈	4.64	43.14	52.22
Highmoor E ₁₁	36.00	64.00
Forest-carex-sphagnum, B.....	6.01	47.41	46.58
Cladium peat, upper layer, D ₂	1.21	38.41	60.38
Cladium peat, drained D ₁	3.16	34.53	62.31
Scirpus peat, F.....	0.72	56.59	42.69
Hypnum, G.....	1.98	58.86	39.16
Dopplerite, H.....	2.89	51.64	35.47
Lake peat, I.....	1.63	64.63	33.74

necessarily in the same sense as that in which the term "humin" is used by protein chemists.

All the horizons of the lowmoor peat profile were entirely free from cellulose, with the exception of the woody material found in some of the lower layers of the profile. On the other hand, the highmoor peat contained con-

siderable quantities of cellulose, especially in the light brown, less decomposed strata. The more compact and darker strata of the highmoor peat, which indicate greater decomposition (E_2 , E_6 , and E_7), contained less cellulose than the less compact and less decomposed strata (E_1 , E_3 , and E_4). The Grenzhorizont and the older sphagnum peat of the highmoor profile contained less cellulose than the younger sphagnum peat. The lowest cellulose content is found in the lowest layer of woody peat, although the particles (E_{12}) of wood selected from this horizon contain considerably more cellulose than the peat itself (E_{11}) showing that these particles of wood have resisted decomposition to a considerably greater extent than the surrounding material.

The partially decomposed, layer of *Cladum* peat contained 5.22 per cent fibrous cellulose, whereas the dark, compact, lower sedimentary layer and the sample of cultivated peat were free from cellulose. The presence of a small amount of cellulose in the layer is due to the great abundance of the roots, partly decomposed and undergoing decomposition. The hypnum and tule peats contain only small amounts of cellulose. It is interesting to note that, although the forest peat (C_1) contained only very little cellulose, the layer of *Sphagnum cuspidatum* peat, surrounded by the forest peat, behaved in this respect like a typical highmoor layer of peat: it was very rich in cellulose, containing 17.94 per cent of this chemical complex.

The lowmoor peat profile was rich in hemicellulose; this was also true of the fibrous *Cladum* peat. However, the highmoor peats contained even larger quantities of this group of polysaccharides than did the lowmoor peats. This group of hemicelluloses is heterogeneous in nature representing only partly pentosans, as brought out in table 5. With one exception, the pentosan content of peat was found to be less than half of the total hemicellulose. The other portion is made up of galactans, mannans, and glucans. In the case of the lowmoor peat, the hemicellulose content diminishes with depth; in the highmoor peat, however, the hemicellulose, as well as the cellulose, contents, are controlled by the nature of the original plant material and the degree of decomposition. The lighter, less compact, and less decomposed strata (E_1 , E_3 , E_4) were much richer in hemicellulose (and cellulose) than the dark-brown, more compact, and more decomposed strata (E_2 , E_6 , E_7). The Grenzhorizont and the older sphagnum peats were lower in hemicelluloses than the younger sphagnum peat.

It is of interest to record in this connection that Von Feilitzen (4) found in the plants of *Sphagnum cuspidatum* 20.8 to 21.42 per cent cellulose and 14.0 per cent pentosan; in a *Sphagnum-Eriophorum* peat, 0.2 to 1.0 m. thick, he found 15.0 to 15.37 per cent cellulose and 12.75 per cent pentosan, while the same highmoor peat contained, at a depth of 1 to 3 meters, 6.64 to 7.1 per cent cellulose and 5.87 per cent pentosan. These results check up very well with the results of the authors on the highmoor peat profile, especially when one recalls that the methods of analysis were distinctly different.

The presence of lignin in peat has been suspected and even demonstrated

by various investigators (5). It has been shown above that the "lignin" content of peat is not fully comparable with the amount of so-called "humic acid" in peat. It should be recalled that, by the term "peat lignin," we understand that part of the peat which is left after treatment with ether, cold and hot water, hot 95 per cent alcohol, boiling for 5 hours with 2 per cent HCl, treatment for 2 hours in the cold with 80 per cent H₂SO₄, then heating under pressure (at 120°C.) for 1 hour with the diluted (5.4 per cent) H₂SO₄. The ash and nitrogen contents ($\times 6.25$) of the residual material are subtracted from the residue to give the lignin content of the peat. The determination of this lignin is a much more accurate index of the nature and amount of peat than is the determination of the "humic acid" content of the peat, or that part of the peat which is soluble in hot NaOH solution and precipitated by HCl. An examination of the lignin content of the different horizons of the peat profiles as well as of the additional peats is very illuminating.

In the case of the lowmoor peat, the lignin content increases with depth until the forest layer is reached (A₁ to A₄). The lake-peat and Gyttja layers contain less lignin than the lowest phragmites and carex layers, partly because of the high ash content of the former and of the different nature of the plant constituents that gave origin to these peats. The lignin content of the woody particles of the peat comprises two-thirds of the total material.

In the case of the highmoor peat, the "lignin" content is considerably higher in the more compact than in the less compact layers; the relative abundance of cellulose and hemicellulose, on the one hand, and of "lignin," on the other, depends more on the nature of the original plants and on the degree of decomposition of the particular stratum rather than upon any particular depth of the peat. However, here as well, we observe a considerably higher lignin in the Grenzhorizont and in the older sphagnum peat than in the younger sphagnum peat. The highest lignin content is found in the woody particles of the lowest horizon.

It is interesting to compare the composition of the wood from the lowest layers of the lowmoor peat from New Jersey (A₇) and from the highmoor peat from Oldenburg, Germany (E₁₂). These results bring out better than do any other data the nature of the processes involved in the formation of peat. These processes include a gradual reduction in the celluloses and hemicelluloses and a gradual increase in the lignin content; the celluloses are reduced from 35–50 per cent in the original wood, to 6–11 per cent; the hemicelluloses are reduced from about 20–25 per cent, to 5–8 per cent; whereas the lignins are increased from 20–25 per cent, to 64–65 per cent.

It is also of interest to compare the composition of the wood (A₇) from the lowmoor Newton peat (at a depth of about 160 cm.—see A₃) with the composition of the peat itself in which the wood was imbedded. The wood is higher in ether-soluble constituents and considerably lower in ash and in protein than the peat itself. The fact that the wood had 6.12 per cent cellulose, while the surrounding peat was free from cellulose, points to its

incomplete decomposition in the wood. The lignin content of the wood is higher than that of the peat surrounding the wood, because of the lower ash content and the presence of cellulose in the woody material. This shows once more that the composition of peat varies considerably and depends upon the nature of the plants from which it has been derived and the processes of decomposition.

Another illustration to the same phenomenon is found in the shallow layer of *Sphagnum cuspidatum* peat (C_2) imbedded in the forest peat (C_1), from which it differs distinctly in composition. The high cellulose and hemicellulose and the low lignin content immediately would place this handful of sphagnum peat with the typical highmoor peats, while the forest peat surrounding this shallow layer of sphagnum in peat is characterized by the presence of only a small amount of cellulose, comparatively little hemicellulose, and a high lignin content.

The more advanced stages of decomposition of the fibrous Cladium peat (table 4) result in the disappearance of the cellulose, reduction of the hemicellulose, and increase in the lignin content. There is also a reduction in the ether-soluble fraction.

The data given in tables 2 (A_1-A_8) and 3 (I) allow us to compare the composition of lake peat and Gyttja layers. These are characterized by a high ash content, a high protein, a low ether-soluble fraction, lack of cellulose, a high hemicellulose, and fairly high lignin content. The Dopplerite is distinctly different in chemical composition from the lake peat. Although it is also free from cellulose and is high in nitrogen and in hemicellulose, it has more ether- and alcohol-soluble materials, is very poor in ash, and is high in lignin.

It may be of interest to discuss at greater length the nitrogen distribution in the different peat materials. The results presented in table 6 show that there is no sharp distinction between the different peats in the distribution of the nitrogen. The only broad conclusion to be drawn from these results is that the more advanced the decomposition of the peat the larger is the amount of nitrogen not readily hydrolyzed by dilute acids. This is seen by a comparison of the different layers of the Newton lowmoor profile and the upper two layers of the highmoor profile (E_1 and E_2). Because the water-soluble nitrogen is rather small in most peats, the increase in the resistant nitrogen corresponds with a decrease in the readily hydrolyzable nitrogen. This fact is of great importance in considering the treatment with acids for the purpose of making its nitrogen more available. A part of the resistant nitrogen can be made soluble when more concentrated acid solutions and a sufficiently high temperature and pressure are used.

When the distribution of nitrogen in peat is compared with that of natural plant materials, it is found that a considerable reduction in the water-soluble

nitrogenous substances and an increase in the amount of nitrogen not readily hydrolyzable by acids have taken place. The mature plants of carex, alfalfa, and even rye straw contain over 20 per cent of their nitrogen in a water-soluble form. Of course, the young growing plants may contain as much as 30 to 40 per cent water-soluble nitrogen. Even mosses, such as sphagnum and hypnum, in a green stage, contain 13 to 20 per cent water-soluble nitrogen, as compared with 1 to 3 per cent of water-soluble nitrogen in the peat. The nitrogen resistant to treatment with comparatively dilute acids, as determined by the above method of analysis, is only about 10 to 20 per cent in the above mentioned plants, and may reach 30 per cent in the case of pine needles. These transformations, namely, the considerable decrease in the water-soluble nitrogen and the increase in the nitrogen resistant to treatment with dilute acids are due to the activities of microorganisms which rapidly decompose the water-soluble substances. The nitrogen made available from the decomposition of the soluble plant constituents is either used by the growing plants, as in the case of sphagnum, or by the microorganisms that bring about the decomposition of the celluloses and hemicelluloses, as in the low-moor peats. New proteins, largely insoluble in water, are thereby synthesized. The explanation for the increase in the nitrogen content of the organic matter from the plant (1.4 per cent nitrogen in carex) to the peat (2 to 4 per cent nitrogen) in the case of the lowmoor and forest peat bogs, and the decrease in the nitrogen from the sphagnum (about 1 per cent nitrogen) to the high-moor peat (0.6 to 0.9 per cent nitrogen), is to be looked for in these processes.

It is interesting to note that 21.67 per cent of the nitrogen of the green parts of carex and only 4 per cent of the nitrogen of the rhizomes were water-soluble, whereas the resistant nitrogen was higher in the latter than in the former. The presence of considerable fungus mycelium in the dead rhizomes accompanied by a considerable reduction of the celluloses and an increase in the protein content point further to considerable decomposition by micro-organisms in the rhizomes.

DISCUSSION

The results presented in this paper bring out most emphatically the fact that the chemical processes involved in peat formation are not the same in different peats, although they may tend in the same direction. The lowmoor and highmoor peats studied most extensively point quite definitely to the nature of the processes involved in both instances.

The lowmoor peat with a vegetation of grasses, sedges, reeds, and shrubs, rich in readily decomposable celluloses and pentosans, is favorable to certain processes which result in the formation of the particular peat. These processes can be summarized as follows: 1. Rapid decomposition of the water-soluble

substances. 2. Comparatively rapid decomposition of the pentosans and celluloses. 3. Resistance of lignins to decomposition and their rapid accumulation. 4. Decomposition of the plant proteins and synthesis of microbial cell substance, finally leading to an accumulation of organic nitrogenous complexes resistant to rapid decomposition, especially under anaerobic conditions. 5. The persistence of certain hemicelluloses, some of which were no doubt formed through the synthesizing activities of microorganisms. 6. Rapid decomposition of the oils, fats, and certain ether-soluble constituents and slow decomposition of the waxes, resins, etc. 7. Drainage of these bogs brings about an abundant development of aerobic actinomyces and bacteria, which lead to a rapid liberation, from the peat complexes, of nitrogen, in the form of ammonia, which is rapidly changed to nitrate and is made available for the growth of cultivated crops.

The formation of an highmoor peat with a vegetation of *Sphagnum*, *Eriophorum*, *Calluna*, etc., rich in resistant hemicelluloses, seems to take place somewhat as follows: 1. A rapid decomposition of a considerable part of the nitrogenous substances present in these plants. 2. A slow decomposition of the carbohydrates of the plants. 3. Because the microorganisms have not sufficiently readily available sources of energy, the nitrogen of the decomposing sphagnum is used immediately by the newly growing plants, thus accounting for the fact that the peat has no more, and even less, nitrogen than the original plant. 4. Slow decomposition and slow but gradual accumulation of the lignins and of the waxy substances. 5. Persistence of the celluloses and hemicellulose for a considerably longer period of time than in the case of the lowland peats. Since these bogs are acid in reaction and are rich in celluloses and hemicelluloses but poor in nitrogen and mineral constituents, before satisfactory crops can be expected drainage and cultivation must be theoretically accompanied by treatment with lime, to neutralize the acidity, and with nitrogenous and other mineral fertilizers necessary for the decomposition of the celluloses and the growth of higher plants.

The following studies which will tend to throw further light upon the problem of peat are at present being carried out in this laboratory: 1. A detailed study of the decomposition of natural plant materials under aerobic and anaerobic conditions. 2. The rôle of microorganisms in peat formation. 3. Decomposition of peat by microorganisms. 4. The nature of certain plant constituents and their resistance to attack by microorganisms.

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BOOK REVIEW

Mycorrhiza. An account of non-pathogenic infection by fungi in vascular plants and bryophytes. By M. C. RAYNER. London, 1927. Pp. vi + 246, fig. 64, pl. 7. (Reprint from *New Phytologist*: 25, 26.)

In this work Mrs. Rayner has given a comprehensive account of the mycorrhiza problem up to and including 1925. This is welcome, as the literature of the mycorrhiza is very extensive and not always easily accessible. The author, thanks to her intimate knowledge of the subject, gained from her researches during many years into the mycorrhiza of *Calluna*, has performed her task in an excellent way.

The contents are well arranged. On a historical basis the author distinguishes three periods; namely, "the early period" (1840-1880), "the second period" (1880 to about 1900), and "the modern period" (1900-1925). As is quite natural, the modern period occupies the main part of the book. In the beginning of this section we find an account of the classical works of Stahl and Bernard. Thereafter, all newer investigations are discussed more or less thoroughly. Quite naturally, the interest is concentrated on the best known types; namely, the mycorrhiza of orchids, heaths, and trees. One chapter is devoted to *Bryophyta* and *Pteridophyta* and one to the tuberisation theory. In her last chapter the author gives a valuable exposition of the physiological significance of mycorrhiza and the nutrition of mycorrhiza plants.

The author points out that in order to obtain a clear idea of the importance of mycorrhiza, it is necessary to study experimentally both symbionts and their mutual relations in pure culture. It is also essential to study the mycorrhiza in their relation to the soil conditions. The author emphasizes the fact that the mycorrhiza formation of trees and of *Calluna* depends greatly on the soil conditions, an important fact, deserving more attention than it has obtained heretofore in the literature. Normal mycorrhiza is not developed by these plants, unless the soil conditions are favorable to the growth of the mycorrhizal fungi. The mycorrhiza formation is consequently the result of the activity of the fungi, as well as of the reaction of the root cells. This means that the mycorrhiza problem is at the same time physiological and ecological.

Earlier experiments, designed to throw a new light on the biology of the mycorrhiza association, were not very successful, partly on account of prevailing ignorance respecting different soil types, and partly because of unsuitable methods for isolating the endophytes. Bernard initiated a new phase of the mycorrhiza researches by making use of bacteriological methods in his studies of the orchid mycorrhiza, and it is at present a known fact that further progress will be gained only by use of similar methods. The author, however, is quite

right in pointing out the necessity of great caution when applying results deduced from pure cultures to the conditions in nature. In cases where the mycorrhiza formation in pure culture will perhaps prove unimportant with respect to the higher symbiont, it may be of vital importance in nature, on account of the competition with the microorganisms of the soil.

After a critical discussion of the experimental mycorrhiza researches of later years, the author concludes that the importance of the mycorrhizal fungi for the higher symbiont is principally the securing of nitrogen in one form or another. In at least two of the three groups of mycorrhizal plants for which experimental data are now available, namely, forest trees and members of *Ericaceae*, modern work has yielded corroborative evidence that this is actually the case. For orchids, the evidence in support of this general hypothesis is, according to the author, less convincing, although there can be no doubt that nitrogenous substances are present in rich abundance in the "Eiwillshypfen," which constitute so conspicuous a feature of the intracellular mycelium within the root tissue.

Logic and clearness of style distinguish the treatise. The figures are well selected and the reproductions exceedingly good. It is impossible to imagine a better summary of the mycorrhiza problem. At the same time, on account of its completeness, it forms an excellent handbook for active workers. Mrs. Rayner's book is a most valuable contribution to the ecological literature.

ELIAS MELIN.

Die praktische Bodenuntersuchung (Practical Study of the Soil). By E. HEINE.

Second edition. Gebrüder Borntraeger, Berlin, 1928. pp. 178, text illus. 26, map 1. Price 7.20 M.

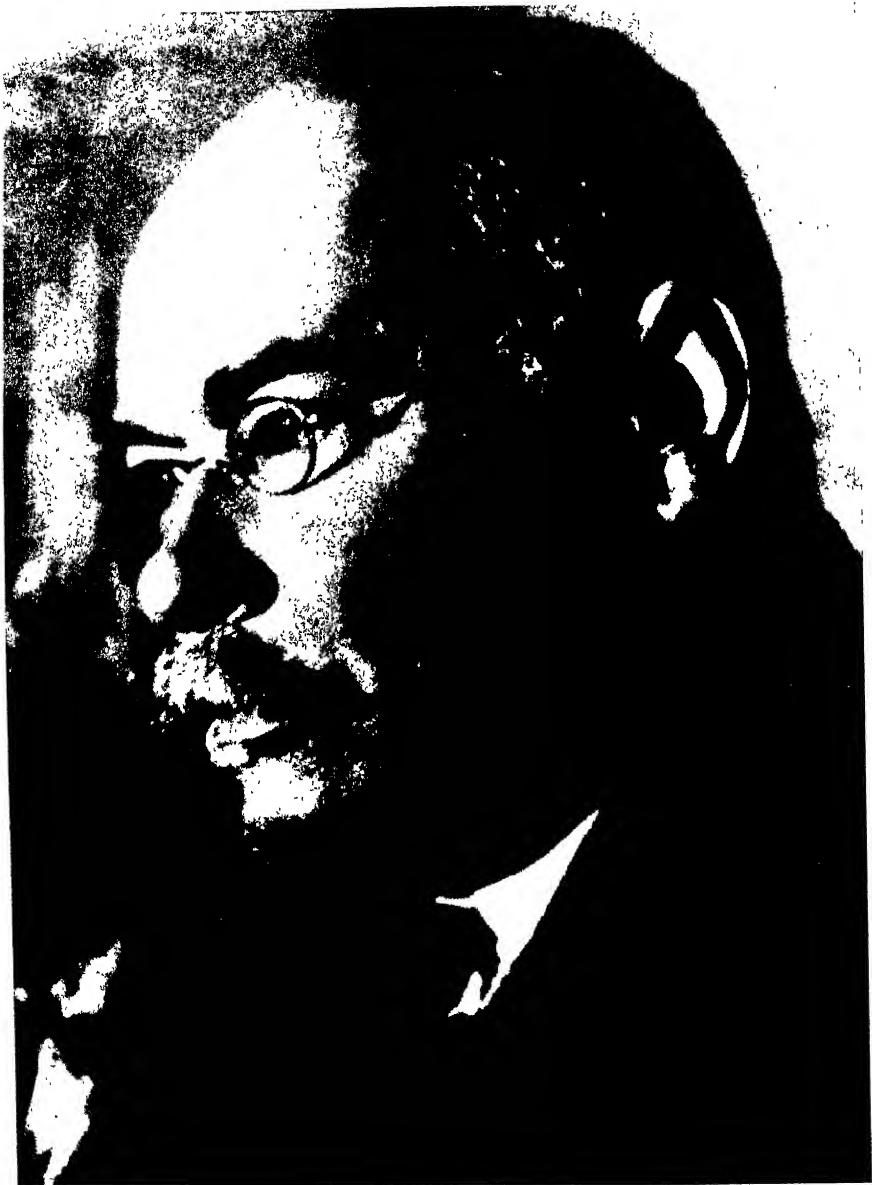
This little volume presents in a very concise manner the available information on soil analysis, which will prove very useful for practical purposes. Its subtitle is "An introduction to the investigation, judgment and improvement of soils, with special relation to the soil types of Northern Germany."

The book is divided into two parts. The first or general part deals with the physical, petrographical, chemical, and biological properties of soils; methods of mechanical and chemical soil analysis; soil classification; and soil amelioration. The second part of the book is devoted entirely to a study of the soils of Northern Germany.

A list of the necessary apparatus required for obtaining soil samples and for carrying out a mechanical and chemical soil analysis is appended.

The text is practically free from references. The 15 titles recommended for supplementary reading are all of German sources.

S. A. WAKSMAN.



PROF. V. L. OMELIANSKY

PROFESSOR V. L. OMELIANSKY

SELMAN A. WAKSMAN

Prof. Vasilii Leonidovitsh Omeliansky, noted Russian bacteriologist, member of the Russian Academy of Sciences, and corresponding member of the Society of American Bacteriologists and of a number of other foreign societies and academies died, on April 21, in Gagri, Caucasia.

With the death of Omeliansky, bacteriology lost an outstanding worker, and Russian science lost one who, following in the footsteps of his noted teacher, Prof. S. Winogradsky, has made the contributions of the Russian bacteriologists famous throughout the world. Omeliansky's outstanding contributions were not only those of a scientist but also of a popularizer, especially in Russia where his textbooks in general bacteriology have gone through numerous editions and where he edited several scientific journals and other publications, including the Archives of Experimental Medicine.

Professor Omeliansky was born on February 26, 1867 in Poltava, in the Ukraine, where his father was instructor of ancient languages. Omeliansky received his primary education in the Zhitomir Classical Gymnasium, of which his father later became director. Omeliansky was graduated from the gymnasium with a silver medal, in 1886, and entered the Natural History Division of the Physico-Mathematical Faculty of the University of St. Petersburg. There he became interested in chemistry and, on graduation from the university in 1890, he continued his studies in organic chemistry, for two years, under Professor Menshutkin.

Because of limited financial circumstances, he had to accept a temporary industrial position as chemist in a metallurgical factory, but he was recalled in 1893 to St. Petersburg to become assistant to Professor S. N. Winogradsky, who was then chief of the division of general microbiology of the Imperial Institute of Experimental Medicine. He assisted Winogradsky in the now famous investigations on the nitrogen-fixing bacteria and on the bacteria bringing about the process of nitrate formation.

In 1895 he began his independent studies on the fermentation of celluloses, which resulted in a series of brilliant contributions dealing with the anaerobic organisms capable of decomposing celluloses. Although he failed to isolate in pure culture the organisms responsible for the process, he has described them very carefully and has established beyond doubt the mechanism of the biochemical transformation of the cellulose.

The first edition of his book "Principles of Microbiology," was published in 1909. This book has gone through six editions, the last one appearing in 1926. During the period of 1911-1916, he carried out a series of investigations on the

fixation of nitrogen by bacteria. These culminated in the publication of his monograph on "The Fixation of Nitrogen by Soil Microbes." The war period resulted in a series of contributions of a practical nature, such as "Bread fermentation," "Preparation of citric acid," "Keffir and Kumiss," "Aroma-producing microorganisms." These were followed by his book "Practical Manual of Microbiology," by a number of popular treatises on bacteriology, by biographies of Metchnikov, Pasteur, and, Winogradsky and by editorial work on the "Progress in biological chemistry," five issues of which appeared before his death. His last work was a book entitled "General and Soil Microbiology," which was completed in December, 1927.

Omeliansky was also professor of bacteriology in the Institute for Women and was well known as a lecturer.

The distinct contribution of Omeliansky to microbiology, in addition to his work on cellulose-decomposing and nitrogen-fixing bacteria, consists of his treatment of microorganisms from a morphological and physiological rather than from an applied point of view. Like his famous teacher, Omeliansky was interested in the microbes as chemical agents, and in their rôle in the transformation of matter in nature.

ON THE MICROSCOPIC METHOD OF STUDYING BACTERIA IN SOIL

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Received for publication May 31, 1928

Several years ago the writer (1) proposed a method for the microscopic examination of bacteria in soil. The technic has recently assumed considerable importance because of its adoption with a few slight modifications by Winogradsky (5) in his "direct method" of studying soil bacteria. The method has been given a more intensive study recently in the writer's laboratory (2, 3) and a few important modifications have been found which both simplify the technic and make it more reliable.

The method depends upon staining dried films of soil on a microscopic slide with one of the dyes of the eosin group, phloxine, erythrosin, or rose bengal. The writer has always preferred rose bengal, although others, including Winogradsky, have preferred erythrosin. The original technic (1) called for a solution of rose bengal in 0.5 per cent phenol. Winogradsky employs a similar phenolic solution of erythrosin. More recently the writer found that still better results could be obtained with one of these dyes if used in plain aqueous solution, provided the soil film before being stained was treated in an acid solution, preferably acetic acid.

A still more recent investigation (3) has shown that the improvement in staining power due to the phenol in the solution or to the acid already on the slide is apparently because of the decrease in the solubility of the dye thus produced. It has also been found that slight variations in the solubility of market samples of the dye, such as might be caused by differences in amounts of mineral impurities present, make considerable difference in the staining ability. This undoubtedly explains why some investigators obtain better results with the technic than others, and possibly explains why one may obtain best results with a certain sample of erythrosin while another has better luck with a sample of rose bengal.

Now that this relation to solubility has been discovered it is possible to employ a simpler technic which at the same time is more sure to give satisfactory results. This technic omits the acid pre-treatment lately recommended, and in addition to phenol in the staining solution prescribes a minute amount of a calcium salt. The presence of the latter partly converts the dye (usually purchased in the form of its di-sodium salt) into the calcium salt which is very much

less soluble than the di-sodium salt. Thus the solubility of the dye in the staining solution is lowered sufficiently to improve the staining power. The phenol is retained in the formula largely as a preservative.

The greater the amount of calcium added (i.e. up to a certain point) the more intense the stain, and it is possible to secure a stain which is too deep. Thus if the dye is dissolved in a solution of CaCl_2 stronger than 0.1 per cent, one is almost sure to find the organic matter in the soil so deeply stained as to obscure the bacteria for which one is looking. With the particular soil and stain sample used by the writer, it was found that the best concentration of CaCl_2 was between 0.01 per cent and 0.03 per cent; but it is quite probable that other dye samples and other soils would require other concentrations of calcium.

The technic now recommended is therefore as follows:

TECHNIC

Gelatin fixative solution. Dissolve 0.15 gm. of gelatin in 1 liter of distilled water with gentle heat. Distribute it in test tubes, 5 cc. or a little more to each tube; plug with cotton and sterilize in an autoclave.

Staining solution. Dissolve 1 gm. of either erythrosin or rose bengal¹ in 100 cc. of a 5 per cent aqueous solution of phenol containing between 0.001 per cent and 0.1 cc. per cent CaCl_2 . The exact amount of CaCl_2 is very important and should be determined in advance for the dye sample used and the soil to be stained; one should employ just enough to give deep staining of the bacteria without too intense coloration of the dead organic matter. Usually such a solution will contain a very faint precipitate of the calcium salt of the dye, which must not be removed but should be brought into suspension by shaking when the staining solution is used.

Procedure. Put 0.5 gm. of soil in 4 to 5 cc. of the gelatin fixative. Mix thoroughly and place a large loopful on a glass microscopic slide, spreading out with a needle until it covers about 1 sq. cm. Let it dry, preferably on a flat surface over a boiling water-bath. Place on it, while the slide is resting on this water-bath, a drop of the staining solution and let it remain for about one minute. Wash off rapidly in water, dry, and examine with high magnification. The writer has found the most satisfactory combination of lenses to be a 1.9 mm. fluorite objective with a 12.5 \times compensating or planoscopic ocular, although other combinations giving similar magnifications and definition can be used.

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¹ The choice between these two dyes is largely one of the shade preferred. Erythrosin gives a red with a slight orange tinge, whereas rose bengal has an equally slight purplish shade.

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SOME COMMENTS ON THE HYDROMETER METHOD FOR STUDYING SOILS

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Certain statements in the latest paper of Bouyoucos on his hydrometer method (1) call for an early reply from the writer. In this paper he deals specifically with the use of the hydrometer for determining (a) the colloidal content of soil and (b) the mechanical analysis of the soil, either in a few groups (sand, silt, and clay) or in a greater number of groups.

The author will not enter into the dispute on the measurement of colloidal content, this has already been taken up by Joseph (3), and recently Gile (2) has put forward some further pertinent considerations. However, the use of the hydrometer for mechanical analysis—or indeed its employment for any kind of observation—necessarily implies the satisfying of certain conditions before the method can be accepted as fulfilling what its sponsor claims for it. In a recent review of progress in soil physics (4) the author pointed out that, in essentials, Bouyoucos' hydrometer method was a determination of density of a soil suspension, and therefore corresponded to an isolated point on the summation percentage curve. The author stated, further, that "the determination was essentially qualitative since an appreciable density difference must exist in the suspension between top and bottom of the long hydrometer bulb after so short a period as 15 minutes." Bouyoucos (1) has now produced figures, and bases thereon the following remarks: "This statement is not justified. The method is quantitative with only a reasonable degree of inaccuracy." To these remarks the author can only reply, in turn, that—assuming such a self-evident fact requires any justification—the existence of an appreciable density gradient in the suspensions is well shown by Bouyoucos' own results. We have only to compare the values (1) given for the hydrometer readings of the top half and lower half of the suspension columns to see this. (See table on following page.)

As the hydrometer is calibrated in grams per liter the figures in the above table are not the actual densities of the suspensions, although these can be obtained by a simple transformation. It is more convenient here to deal with the former values. The results show differences in hydrometer readings between top and bottom halves of the same suspension of between 10 and 30 per cent, depending on the soil and the time of standing, and it must be remembered that in each case these values refer to the average of many different depths of

EXPERIMENT AND TIME OF STANDING	READING, UNDISTURBED COLUMN	DIFFERENCE IN READING, TOP AND BOTTOM HALF	DIFFERENCE IN READING, AS PER CENT OF UNDISTURBED COLUMN
	gm. per liter	gm. per liter	
1. Clay, 4 days.....	23.20	8.00	29.0
2. Clay, 2 hours.....	28.12	2.80	10.0
3. Clay, 15 minutes.....	36.17	3.43	9.5
4. Silt loam, 4 days.....	18.5	4.2	23
5. Silt loam, 2 hours.....	24.3	4.1	17
6. Silt loam, 15 minutes.....	29.4	3.9	13
7. Loam, 24 hours.....	10.5	3.0	27
8. Loam, 2 hours.....	12.2	1.4	11
9. Loam, 15 minutes.....	16.0	3.9	24

suspension. The actual density differences between the top and bottom layers of the whole column will be of course, very considerably greater than those corresponding to the above figures.

Bouyoucos also lays stress on the fact that the mean of the hydrometer readings for the upper and lower halves of the column is about equal to that of the undisturbed column, and considers that these results "refute the contentions or criticisms advanced by Joseph and Keen." It is evident, of course, that the average density of the suspension in the region where the hydrometer comes to rest in the original column of suspension will have a value intermediate between that of the superincumbent layers and that below the hydrometer, and in view of the averaging effect of the long hydrometer bulb employed it is not surprising that this intermediate value approximates to the mean. But the result has no other significance: it merely demonstrates the fact that a gradient of increasing density exists from top to bottom of the suspension. This density variation at different depths of the suspension is not constant, but progressively changes with time while the particles are slowly settling, and the actual manner in which it changes with time depends on the size distribution curve of the soil, and therefore varies from one soil to the next. Hence some convenient time has to be selected and laid down in the details of the method as the one to be used if comparable data are to be secured. The selection of 15 minutes, for example, is entirely arbitrary; this interval allows most of the coarser material to fall below the hydrometer range.

Hence in physical terms, the hydrometer technique consists in measuring at an arbitrary time the average density of a layer of suspension several centimeters in length, whose density is continually changing both with depth and time. The statement that the method is "essentially qualitative" is not a matter of personal opinion, but of fact.

Apart from this aspect it would appear that Bouyoucos has also not fully considered the inevitable disturbance produced in the mechanism of the

sedimentation by the presence of the hydrometer itself. Such disturbances are unfortunately inherent in all methods based on density or hydrostatic pressure measurements in a suspension. The reason for this was given in sufficient detail in a recent review (4) and need not be mentioned again.

It is evident that in spite of these facts the experimental results can, with due precaution, be repeated with very reasonable accuracy. (The results with the loam soil in lines 7-9 of the foregoing table, showing a minimum difference in density of top and bottom halves after 2 hours standing, in contrast to the regular increase with the other two soils, point at first sight to a rather considerable degree of inherent error; but this particular result may probably be fairly ascribed to some accidental disturbance). However, accurate repetition of a given result does not turn a qualitative method into a quantitative one, if we retain, as we ought, the strict meaning of these words.

In writing the foregoing, the author's only concern is that soil physics should have something of the precision of theory and experiment associated with the science of pure physics. Bouyoucos, in his legitimate enthusiasm over the experimental results of the hydrometer method, has implicitly claimed a fundamental basis for what, by its very nature, can only be an empirical method.

This is not intended in the least to deny its value as an empirical method. Bouyoucos has shown great skill in devising his apparatus and technique so that certain experimental errors are either nullified or mutually compensate one another, and in the present stage of development of soil physics the close relation of the results to those given by other empirical methods is a distinctly useful addition to our knowledge.

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DESIRABLE SOIL-NITRATE LEVELS FOR CERTAIN MARKET-GARDEN CROPS¹

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Observations have indicated that the small quantities of nitrates commonly found in soils supporting luxuriant growths of grasses are not sufficient for the current needs of market-garden crops. If this be true, it seems probable that rather definite minimum concentrations of soil nitrates should be maintained or exceeded for the production of satisfactory growth, and that the minima may vary for different types of plants.

Significant positive correlations have often been noted between soil-nitrate concentrations and the growth and yields of crops, but few attempts have been made to define optimum concentrations. Arrhenius (1) has concluded that 9.5 p.p.m. of nitric nitrogen is the optimum level to be maintained under oats, barley and sugar beets, but that this concentration need be present only during the first six weeks of growth.

Nitrogenous fertilizers are probably most effective at definite growth stages, but there is also evidence that the most satisfactory yields of field-grown vegetable-crop plants are secured by a constant supply of this element throughout the life of the plant. Barrow, Morgan, and Burnette (2), working with complete fertilizers for cabbage, tomatoes, potatoes, and corn; and Voorhees (11), using side-dressings of nitrate of soda for celery and cucumbers, reported progressive increases in yields when the same total amount of plant food was applied in one, two, or three applications during the season. Edmond and Lewis (3) found earlier maturity for cabbage supplied with complete fertilizer at three successive stages of growth from seedling to harvest, but no significant increase in yield over plants supplied with a like total amount at any one period or combination of two periods. It appears probable that there is a constant demand for nitrogen throughout the life of the plant, but that the intensity of the demand is greater at different stages of maturity.

The object of the work here reported was to seek further instances of correlation between yields of market-garden crops and nitrate concentrations in the soil, and to propose a tentative desirable nitrate level for each crop studied.

¹ Contribution No. 367 of the station.

² Associate Chemist.

The writer is indebted to Dr. B. L. Hartwell and Dr. B. E. Gilbert for advice, and to F. K. Crandall, under whose supervision the crops were grown.

Future studies will determine the sufficiency of these levels to supply the immediate needs of the crop at all stages of growth.

For the purpose of this preliminary study, nitrate nitrogen has been selected as the measure of the available nitrogen under normal soil conditions, despite the demonstrated absorption of other forms of nitrogen by plants. This is in accord with the conclusions of Russel (9), of Fraps (5), and others. The writer has shown (10) that in two field plats of like degree of acidity, sulfate of ammonia, applied April 2, was nitrified so rapidly that the nitrate accumulated by April 27 was practically equal to that produced by an equal application of nitrogen in nitrate of soda. It appears probable that the rapid rate of nitrification of ammonia in normal humid soils places so large a proportion of the available nitrogen in nitrate form that soil ammonia need be considered only when nitrate accumulations are of very small magnitude. This assumption will be tested in a continuation of the study.

CHEMICAL METHODS

The soil was sampled to the plowing depth, approximately 7 inches, borings being taken directly in the rows of drilled crops, and within 6 inches of plants spaced singly. Fifteen borings were composited to represent areas of 1/30 acre, and the composite samples were passed through a 5-mesh sieve. In 1927, water extracts were prepared and nitrate nitrogen was determined by the Harper modification of the phenoldisulfonic acid method (7), and in 1926 from 2 to 3 gm. of calcium oxide was used as a clarifying agent in place of the reagents recommended by Harper. The water extracts were prepared and aliquots sterilized by evaporation on the steam bath within 24 hours from the time that the samples were taken in the field. The color comparisons were made in a Campbell-Hurley colorimeter, and the results reported as parts per million of nitric nitrogen in oven-dry soil.

EXPERIMENTAL CONDITIONS

The soil of the permanent field plats used was classified and renamed in 1913 by the U. S Department of Agriculture as Merrimac silt loam, mellow and friable at the surface and underlain by a plastic yellow silt loam. This plastic layer is a beneficial factor in preventing leaching from the surface into a substratum of coarse gravel. The field area is level, the soil appears uniform, and the 1/30 acre plats are of sufficient size to give significance to important differences in crop yields.

Optimum amendments and fertilizers were used in accordance with agronomical experience with this soil, except that nitrogen additions were reduced or withheld from areas intended to be suboptimum for this element. All fertilizer applications discussed in this paper have been reported on the acre basis.

Climatic data, crop yields, and observations of plant growth indicate the growing seasons of 1926 and 1927 to have been satisfactory. Fifteen inches of

rainfall between May 1 and October 1, 1926, were adequate for the crops studied, since only late celery benefited by the 30 inches of rain that fell within the same period in 1927. This 30-inch rainfall caused decided leaching between August 8 and September 13, and resulted in depressed growth of late beets.

In table 1 is shown the relation of the soil moistures to the water-holding capacity of the soils of the plats studied. For the two seasons the minimum moisture found was equivalent to 33 per cent of the water-holding capacity, and the maximum was 57 per cent. The mean for 1926 was 42 per cent and

TABLE 1
Summary of soil moistures, May to October, expressed as per cent of the water-holding capacity satisfied

WATER-HOLDING CAPACITY SATISFIED	ORGANIC MATTER TREATMENTS			
	None	16 tons manure	32 tons* manure	Various green manures
<i>1926</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
Minimum.....	..	35	33	33
Maximum.....	..	52	38	50
Mean.....	..	44	40	42
<i>1927</i>				
Minimum.....	37	45	44	44
Maximum.....	57	54	49	55
Mean.....	53	50	46	50
Water-holding capacity, per cent of dry soil.....	56	69	80	63

* Only 24 tons in 1927.

that for 1927, 49 per cent. None of these values lie outside a satisfactory range for the water needs of crops in general. Water-holding capacity was determined by the method described by Fraps (4).

Soil temperatures in 1926, read for the top 3 inches of soil before 8 a.m., rose slowly to 60°F. on June 25, fluctuated between that level and 70°F. until September 9, and fell gradually to 40°F. on October 29. In 1927, the first two corresponding temperatures were reached on June 30 and August 30, respectively, whereas the autumn temperatures were somewhat warmer than those of the previous year. Late afternoon temperatures in the same soil were higher by approximately 10°F.

The writer has shown (10) that the climatic factors prevailing at this station are favorable to satisfactory production of nitrates from normal soil treatments. Nitrate accumulation, although accelerated by liming, was not found to be a

limiting factor for the growth of most crops at a degree of acidity below a pH of 5.0. Normal applications of phosphatic fertilizers were sufficient for maximum nitrification. Spring applications of stable manure containing considerable straw did not increase the rate of nitrification early in the season, but no serious depression was noted.

RESULTS

The plan of the experiment

It was arranged to compare the yields of certain market-garden crops at a high soil-nitrate level, produced by 16 tons of horse-stable manure liberally supplemented by complete chemical fertilizers, with a possible suboptimum level obtained by the partial omission of nitrogen from the chemical supplement. Certain of the crops were also grown following the plowing in of green manures, both with and without optimum nitrogen in the fertilizer chemicals added.

The plats and crops were those of a permanent three-year market-garden rotation established in 1916, and described by Hartwell and Crandall (8). In this rotation, cabbage, tomatoes, and lettuce grown in the spring are followed in late summer by beets, spinach, and celery, respectively. A $\frac{1}{10}$ -acre plat is devoted to each treatment for each crop. Prior to 1926, the nitrogen comparison was between optimum and superoptimum treatments. Despite the large amounts of nitrogen that had been used in the superoptimum treatment, the omission of that element from the fertilizer supplement for those plats in 1926 depressed growth to the extent that side-dressings were necessary. By this change, the extra nitrogen plats became the suboptimum areas reported in this paper.

The spring applications of manure were accumulated during the previous winter and contained considerable amounts of straw. In 1927, a compost of horse-stable manure and vegetable refuse was substituted for the manure in quantities expected to furnish an equivalent amount of organic matter. Fertilizer supplements were applied in the spring and before planting the second crop at midsummer. In addition, side-dressings of soluble nitrogen were applied as the need was indicated by depletion of nitrate accumulations in the soils of the suboptimum plats, or by excessive depression of growth. All soil treatments and crop yields are reported on the acre basis.

The naturally acid soil had been limed to a pH of approximately 7.2 in 1926, and 7.6 in 1927. The use of manganese sulfate, either as an ingredient in the fertilizer or as a spray, efficiently counteracted a lime-induced chlorosis previously reported by this station (6). The exception was chlorotic growth of late beets in 1927.

Early cabbage

Golden Acre cabbage plants were set the third week in April in soil last manured before lettuce in the spring of the previous year, and in soil con-

NITRATE LEVELS FOR MARKET-GARDEN CROPS

TABLE 2
Nitrate nitrogen in surface soil under cabbage

TREATMENT	MANURE	CHEMICALS†		NITRATE NITROGEN						YIELDS OF HEADS		
		N	P ₂ O ₅	K ₂ O	May 25	June 3	June 13	June 17	June 22	June 30	Total barrels** per acre	Before July 11 barrels*** per acre
		<i>tons</i>	<i>pounds</i>	<i>pounds</i>	<i>p.p.m.</i>	<i>p.p.m.</i>	<i>p.p.m.</i>	<i>p.p.m.</i>	<i>p.p.m.</i>	<i>p.p.m.</i>		
		<i>pounds</i>										
<i>1926</i>												
Standard.....	16*	100	200	100	18	18	11	578
Low N.....	16*	20§	200	100	3	26	10	466
Standard.....	Oats†	100	200	100	16	14	7	453
Low N.....	Oats†	20§	200	100	2	23	8	360
<i>1927</i>												
Standard.....	16*	130**	200	100	37	19	8	584
Low N.....	16*	60††	200	100	10	4	6	521
Standard.....	Oats†	130**	200	100	..	34	18	24	551
Low N.....	Oats†	60§§§	200	100	..	6	6	6	530
												80

* Applied before lettuce in the spring of the previous year.

† Plowed in as a green manure in the spring of the previous year.
‡ First applications April 21, 1926, and April 15, 1927.

§ As a side-dressing, May 27.

** Includes side-dressing, June 15, 30 pounds.

†† Includes side-dressings, June 9, 15 pounds; June 15, 15 pounds.
§§§ Includes side-dressing, June 9, 15 pounds.

*** 80 pounds.

TABLE 3
Nitrate nitrogen in surface soil under tomatoes

TREATMENT	CHEMICALS†		NITRATE NITROGEN						FRUITS				
	MATURE TONS	N P ₂ O ₅	K ₂ O	May 25	June 13	June 17	June 30	July 17	July 21	August 3	August 8	Total green- ripe per acre	No. 1 ripe before August 16 per acre
<i>1926</i>		<i>pounds</i>	<i>pounds</i>	<i>p.p.m.</i>									
Standard.....	16*	60	200	30	..	38	..	34	..	48	..	336	23
	16*	20§	200	30	..	8	..	14	..	40	..	182	15
Low N.....													
Standard.....	Rye†	50	200	100	40	..	128	..	68	..	23	647	36
	Rye†	20§	200	100	6	..	16	..	8	..	14	596	23
<i>1927</i>													
Standard.....	16*	60	200	30	..	93	..	50	..	23	..	5	407
	16*	35	200	30	..	72	..	26	..	6	..	5	387
Standard.....	Rye†	100	200	150	..	189	..	67	..	15	..	10	477
	Rye†	60	200	150	..	93	..	30	..	10	..	5	333
Low N.....													

* 1926, horse stable manure; 1927, manure compost equivalent in weight of organic matter to 16 tons of manure.

† Buckwheat followed by rye; both crops plowed in as green manure.

‡ 1926, applied one half May 19, remainder June 22; 1927, applied one half May 18, remainder July 14.

§ As a side-dressing, June 22.

** 56 pounds.

taining oats green manure. Only the chemical supplements were used immediately before cabbage. These are reported with the resulting yields and accompanying nitrate determinations in table 2.

The character of growth on the standard, or optimum, plats was uniformly good and the total weights of heads, picked as they matured between June 28 and July 21, were greater than the average for the first nine years of the rotation (8). The loss of a group of plants representing 10 per cent of those set on the standard stable-manure plat in 1927 was corrected by substituting smaller plants to occupy the space, and adding the probable weights of the lost heads to the harvest weights.

The effects of different levels of soil nitrates on yields of this variety of cabbage were best observed in 1927. A level of nitrate nitrogen below 10 p.p.m. was equal to one of approximately twice that concentration for total yields, but so retarded maturity that the weights of the first two pickings were reduced by one-third. This is a material economic loss when earliness is a decisive factor in price determination. Retarded maturity from nitrogen starvation was more marked in 1926, although the contrast of the two levels of nitrates was obscured by a midseason side-dressing for the suboptimum treatment. A low nitrate concentration in May reduced the yield of marketable heads picked before July 11 by more than 85 per cent and the total yields for the season by nearly 20 per cent. These results are in general agreement with those of Edmonds and Lewis (3).

It appears desirable to maintain soil-nitrate concentrations under cabbage well above the 15 p.p.m. level when earliness is a required factor; otherwise, a 10 p.p.m. level is probably sufficient.

Early tomatoes

Tomato plants were set May 19 on plats that had received stable manure and on plats containing green manure from fall-plowed buckwheat followed by rye turned under in the spring. One-half of the fertilizer supplement was mixed with the soil about the plants at the time of setting and the remainder was distributed about the growing plants on June 22, 1926 and July 14, 1927. Equal numbers of plants of the Earliana and of Murry's New Early Wonder varieties were grown in 1926, but only the latter variety in 1927.

Fruits were picked as they ripened after July 17, 1926 and July 30, 1927. This method of harvesting was continued until late in August, when all the remaining fruits were gathered. The total yields reported include both ripe and green fruits, as classification according to size and degree of ripeness did not materially change the relations among the different treatments. Only the weights of the first six pickings are separated from those of the completed harvest.

Data relative to fertilization, yields, and nitrate accumulations noted are reported in table 3. From an undiscovered cause, the yields from the stable-manure areas were less than one-half of those expected for this rotation. In

contrast, unusually luxuriant vine growth on the standard green-manure plat brought yields materially greater than the nine-year average for that treatment (8). This was especially true in the better tomato year, 1926. A positive correlation between vigorous vine development and yields of fruits appears to be characteristic of these tomato varieties.

Attention is directed to the results from the low-nitrogen green-manure area of 1926, the only successful attempt at maintenance of a uniform level of soil nitrates under a satisfactory tomato crop. A nitrate level of 8 to 16 p.p.m. accompanied a 596-bushel yield, and concentrations seven-fold greater, maintained until the time of the first picking, hastened maturity, but did not increase total yields. For the same treatments in 1927, an accumulation of 10 p.p.m. of nitrate nitrogen on August 8 proved superior to a lesser concentration after July 21 on an adjacent area.

Little confidence can be placed in relationships between soil nitrates and the subnormal yields from the stable-manure areas, despite the considerable degree

TABLE 4
Nitrate nitrogen in surface soil under lettuce, 1927

TREATMENT	CHEMICALS*			NITRATE NITROGEN			YIELDS OF HEADS			
	N	P ₂ O ₅	K ₂ O	June 8	June 13	June 30	Cwt. per acre	Boxes (18 heads) per acre		
				pounds	pounds	pounds		No. 1	No. 2	Total
Standard.....	60	200	30	31	21	3	164	603	1,157	1,760
Low N.....	0	200	30	18	9	12	159	507	1,278	1,785

* Applied April 13, after the plowing in of manure compost containing organic matter equivalent to that in 16 tons of manure.

of correlation that existed. It is evident that some other factor was chiefly responsible for the depressed growth, as greater yields were secured from green-manure plats where the nitrate accumulations were less.

Subject to future correction, a tentative desirable soil-nitrate level for the production of early fruits from the tomato varieties mentioned is placed at 20 p.p.m.

Lettuce

Black-seeded Tennisball lettuce (table 4) was planted April 13, 1927, and harvested between June 28 and July 7. Although this leafy crop might be expected to respond to nitrogen, the addition of 60 pounds of that element to the equivalent in organic matter of 16 tons of stable manure has failed to improve lettuce yields for the second consecutive trial. The results of one season indicate that a level of 10 p.p.m. of nitrate nitrogen maintained throughout the growing season is sufficient for this crop.

TABLE 5
*Nitrate nitrogen in surface soil under beets**

TREATMENT	MANURE†	CHEMICAL‡		NITRATE NITROGEN						YIELDS OF ROOTS PER ACRE	
		N	P ₂ O ₅	KO	August 8	August 17	August 24	September 13	September 27	October 8	October 24
	tons	pounds	pounds	pounds	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.	bushels
1926											
	Standard.....	16	90§	120	90	14	13
1927	Low N.....	16	45**	120	90	5	10
	Standard.....	16	115††	120	90	45	6	..	2	4	452
	Low N.....	16	63††	120	90	31	4	..	2	3	334

Following cabbage, table 2.

Applied before lettuce in the spring of the previous year.

First applications July 23, 1926; July 26, 1927.

Includes 20 pounds as a side-dressing September 9.

* Includes 35 pounds August 26; 10 pounds, September 9.

† Includes 15 pounds as a side-dressing on each of the following dates; August 19, September 2, September 5.

‡ Side-dressings equal to one half those of the standard treatment.

§ 50 pounds.

Beets

This crop was planted late in July, following cabbage grown with stable manure and chemicals as already described (table 2). The chemical supplements used before the beets are reported in table 5, as are the yields secured and the nitrate accumulations observed. Seeds of the Crosby's Dark Egyptian and Early Wonder varieties were sown together in 1926, but equal areas were devoted to each variety in 1927. The beets were pulled late in October.

An application of 30 pounds of manganese sulfate with the fertilizer chemicals for cabbage in 1926, followed by 15 pounds in a solution sprayed on the beets, successfully overcame a lime-induced chlorosis and doubled the yield expected from this rotation (8). In 1927, however, the 30 pounds of manganese sulfate applied with the fertilizer was ineffective, although the salt was used immediately before the beets rather than before the cabbage, and an additional 10 pounds in solution sprayed on the plants September 15. This lack was demonstrated by a significant increase in the yield where 30 pounds of the salt was applied in two sprayings on one-half of an adjacent plat that had also had the initial application of 30 pounds with the fertilizer. Excessive leaching from the heavy rains of August and September reduced soil nitrates for both the standard and the low-nitrogen plats to a lower level than that which was suboptimum the previous year.

For the better season, 1926, a nitrate level of 10 p.p.m. accompanied a satisfactory growth, whereas one averaging little more than one-half that magnitude, reduced the yield by 25 per cent. A nitrate level below 10 p.p.m. appears to be undesirable for late beets.

Spinach

Savoy-leaved spinach was planted about September 1 and harvested before October 11, 1926 and October 26, 1927. The plats were those from which early tomatoes had been removed (table 3), and had received a spring application of 16 tons of manure or an equivalent quantity of organic matter in manure compost. Fertilizer supplements, applied in the spring and again before the spinach was planted, were arranged to provide a standard and a low-nitrogen ration. The use of manganese in solution successfully prevented injury from the lime-induced chlorosis that has inhibited the growth of spinach in the past, and very satisfactory yields were obtained.

Nitrate-nitrogen concentrations, reported in table 6, were relatively high until the approach of the harvest, and were in close agreement on September 27 of the two years, when accumulations of approximately 45 p.p.m. and 25 p.p.m. existed in the soil of the standard and low-nitrogen plats, respectively. The relations observed between nitrate concentrations and spinach yields were contradictory in that there was no benefit from the greater level in 1926, whereas the 1927 crop was increased 13 per cent. The contradictory data do not justify the selection of an optimum nitrate concentration for 'Savoy-leaved' spinach, but a level below 20 p.p.m. does not appear advisable.

Celery

Plants of the Golden Plume variety were set the third week in July, and cut two or three weeks after being boarded early in October. This crop followed lettuce grown with stable manure and chemicals as described in table 4; also oats, timothy, and rye green manures. All sources of organic matter were supplemented by chemicals, and two levels of nitrogen fertilization were provided both for the stable manure and for the oats green manure. Growth and yields were satisfactory, especially in 1927 when the wet season proved very favorable to this crop. As is characteristic of the rotation, slow development of the newly set plants on the green-manure plats retarded the growth, but the yields obtained were materially larger than the nine-year average for the green-manure treatments of this rotation (8). Blight injury was success-

TABLE 6
*Nitrate nitrogen in surface soil under spinach**

TREATMENT	MA-NURE†	CHEMICALS‡			NITRATE NITROGEN					YIELD PER ACRE
		N	P ₂ O ₅	K ₂ O	Septem-ber 13	Septem-ber 15	Septem-ber 27	Octo-ber 8	Octo-ber 24	
	tons	pounds	pounds	pounds	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.	bu.§
<i>1926</i>										
Standard.....	16	70	120	90	..	60	44	34	..	1,320
Low N.....	16	35	120	90	..	26	22	8	..	1,395
<i>1927</i>										
Standard.....	16	70	120	90	37	..	46	..	4	1,548
Low N.....	16	30	120	90	20	..	26	..	2	1,368

* Following tomatoes, table 3.

† Applied in spring, before tomatoes; 1926, horse stable manure; 1927, organic matter in manure compost equivalent to that in 16 tons of manure.

‡ Applied August 27, 1926; Applied September 2, 1927.

§ 12 pounds.

fully checked by frequent sprayings with Bordeaux mixture. Samples of the crop taken at harvest were analyzed for nitrogen by standard methods. Data relative to celery are reported in table 7.

Various levels of nitrate are presented for study, but attention is directed chiefly to the comparison of 120 pounds versus 60 pounds of soluble nitrogen, each used with 16 tons of stable manure in 1926. The lesser quantity of nitrogen maintained a rather uniform level of nitrate nitrogen averaging 5 p.p.m. on the sampling dates, although the 5 and 10 p.p.m. increases that resulted from side-dressings contained 10 and 20 pounds of nitrate nitrogen on August 19 and September 7, respectively, may have given a level temporarily above that limit. As compared with this low level, nitrate concentrations that were three times higher on the sampling dates increased the yields by only 15 per cent, and

TABLE 7
Nitrate nitrogen in surface soil under celery

TREATMENT	MANURE	CHEMICALS†			NITRATE NITROGEN												YIELD UN- TRIMMED PER ACRE	NITROGEN IN DRY MATTER OF CROP per cent	
		N	P ₂ O ₅	K ₂ O	July 21	August 3	August 8	August 16	August 30	August 31	Septem- ber 13	Septem- ber 27	Octo- ber 8	Octo- ber 27	Octo- ber 27	Octo- ber 27	Octo- ber 27		
	tons	pounds	pounds	pounds	pounds	pounds	pounds	pounds	pounds	pounds	pounds	pounds	pounds	pounds	pounds	pounds	pounds		
1926																			
Standard.....	16*	120\$	120	90	..	28	..	18	12	..	28	339	3.20	72	
Low N.....	16*	60**	120	90	..	8	..	5	4	..	5	294	2.87	53	
Standard.....	Oats†	120\$	100	200	..	39	..	32	25	..	38	194	3.09	44	
Low N.....	Oats†	60**	100	200	..	19	..	11	10	..	10	257	2.76	57	
Standard.....	Timothy†	120\$	100	200	..	25	..	15	13	..	18	239	2.84	45	
Standard.....	Rye†	120\$	100	200	..	31	..	25	14	..	28	230	2.91	54	
1927																			
Standard.....	16*	100	120	90	16	..	20	..	14	6	..	4	9	8	394	2.72	69
Low N.....	16*	65	120	90	5	..	18	..	6	3	..	3	6	10	395	2.76	64
Standard.....	Oats†	110	200	150	16	..	22	..	9	4	..	4	5	15	266	3.60	42
Low N.....	Oats†	75	200	150	6	..	11	..	6	2	..	3	2	8	320	2.80	59
Standard.....	Timothy†	110	200	150	10	..	20	..	10	2	..	2	4	9	322	2.59	43
Standard.....	Rye†	110	200	150	22	..	28	..	10	2	..	3	8	343	2.84	64

* Applied before lettuce in the spring. 1926, horse-stable manure; 1927, manure compost equivalent in weight of organic matter to 16 tons of manure.

† Plowed in for green manure. Fall-plowed rape preceded the oats.

‡ 1926, first application July 17. In 1927, P₂O₅ was applied July 9, and N and K₂O in three equal applications August 2, 19, and September 2, except that standard treatments had 30 pounds of N on September 20 when the low N plots had 15 pounds.

§ Includes side-dressings of 20 pounds July 17; 20 pounds August 19; 40 pounds September 7; 40 pounds September 24.

** Includes side-dressings of 20 pounds August 19; 40 pounds September 7.

a relatively high percentage of nitrogen in the dry matter of the larger crop gave a degree of assurance that more nitrogen would not have brought further increase. In the following year, when the celery possibility was greater, heavy rains prevented control of the nitrate levels, and the concentrations compared were much alike, averaging 11 p.p.m. and 7 p.p.m. As a result, the yields, the percentages of nitrogen in dry matter, and the quantities of nitrogen removed by the crop were almost identical for the two areas. It cannot be assumed that greater nitrate concentrations would not have increased the growth. For the average season, however, it does not appear that concentrations greater than 10 p.p.m. are needed for this type of celery.

For the first nine years of the rotation, the average yield of celery for the best green-manure treatment was but two-thirds of that from the most favorable stable manure supplement. As has been stated, this was due to delayed recovery from the effects of transplanting. Plants on the green-manure soils have remained yellow and without vigor for two weeks after those on the stable-manure plats exhibited a healthy green color. As a possible factor contributing to this condition, the nitrate relations between green manures and the celery were studied.

Rye, timothy, and oats were plowed under about May 20, June 10, and June 30, respectively. The rye and timothy were planted the previous summer, following tomatoes, and were supplied with 50 pounds of fertilizer nitrogen when planted and an equal quantity the next spring; also liberal quantities of phosphoric acid and potash. Oats were planted in the spring in soil where rape, grown at the same time as the rye and timothy, had been turned under the preceding fall. In addition to phosphates and potash, the rape on the standard plat had 50 pounds of nitrogen, as did the oats that followed; but the rape on the low-nitrogen areas received but 25 pounds of nitrogen in 1926 and both crops of low-nitrogen oats were grown without fertilizer nitrogen.

Analyses of oats cut from representative areas of 1 square yard each, show that approximately 2500 pounds of dry matter containing 75 pounds of nitrogen were turned under in 1926, both on the standard and on the low-nitrogen plats. In 1927, however, 3800 pounds of dry matter grown on the standard plat contained 70 pounds of nitrogen, whereas 3500 pounds on the low-nitrogen area had but 46 pounds of that element. The rye and timothy produced less dry matter than did the succession of rape and oats, and were less nitrogenous than the oats. In 1926, the nitrogen percentages in the dry matter of the different crops were as follows; standard-nitrogen oats 3.17, low-nitrogen oats 2.82, rye 1.60, timothy 1.51.

In accordance with the findings of Waksman (12) and others, the rates of decomposition and subsequent nitrate accumulation were greatest for the crops with the highest nitrogen percentages. Previous work with this rotation (10) demonstrated that nitrate accumulations were greatest after the oats, followed by rye and timothy in the order of decreasing percentages of nitrogen in the crop. These differences were largely masked by the fertilizer nitrogen

applied for the celery, but nitrate concentrations under the growing celery and the quantities of nitrogen removed by the crop (table 7), show rye to have been superior to timothy as a source of available nitrogen. The celery was not improved by the increased supplies of nitrates from the more nitrogenous green manures.

The relations between oats green manure and celery are of interest, in that, for three consecutive years, an increased percentage of nitrogen in the oats has decreased the yields of celery. The growth depression was not due to nitrogen starvation, nor was it correlated with the quantities of green manure used. For the years reported in table 7, the depressed crops of celery absorbed 20 per cent less nitrogen than did those grown on less nitrogenous oats green manure, but the percentage of nitrogen was significantly greater in the smaller crop, a condition consistent with luxury consumption of nitrogen. Also, the soil-nitrate accumulations were greater under the smaller crops, showing that the supplies of available nitrogen were not used. When approximately equal weights of oats were turned under for the standard and the low-nitrogen areas of 1926, the celery yields were 194 cwt. and 257 cwt., respectively. In 1927, 3800 pounds of oats dry matter did prevent a better yield of celery than that from 2500 pounds in 1926.

The increased rate of decomposition of the more nitrogenous oats was demonstrated strikingly when the plats were plowed after the oats had been mixed with the soil for nearly a year. In the spring of 1928, there was almost no undecomposed residue visable in the soil of the standard plat, but a considerable quantity of oat stems was recognizable on the low-nitrogen area. Nitrogen percentages in the dry matter of the two crops were 1.85 and 1.34, respectively; but it should be noted that decomposition from the standard treatment was favored by an excess of 35 pounds of nitrogen in the fertilizer supplement (see table 7). Nitrogen was not determined in the dry matter of the rye and timothy grown in 1927 but the disappearance of these crops was intermediate between that of the two crops of oats.

The detrimental factor was not determined, but it seems possible that hastened decomposition of the more nitrogenous oats accelerated the release of a product that accumulated in toxic concentrations, or modified materially the degree of soil aeration at the critical period for the growth of celery. On the other hand, delayed decomposition of less nitrogenous oats postponed damaging accumulations beyond the critical period.

GENERAL DISCUSSION

It might be assumed that the rate of nitrogen absorption by the crop could be balanced by an equal rate of nitrification and that the nitrate needs of plants could be supplied without appreciable accumulation of the nutrient in the soil. Such may be true for the grasses, but does not appear to hold for vegetable crops. Aside from the little-known factors that govern the absorption of nutrients, it is suggested that the roots of the latter type of plants do not

permeate the soil so completely as do those of the grasses, necessitating movement by diffusion to bring nitrates in contact with the root hairs. Obviously such movement would be more abundant from the larger nitrate accumulations.

SUMMARY

A two-year study was made of the relations between soil-nitrate concentrations and the yields of the six vegetable crops comprising a market-garden rotation. As a result of the study, the following levels of nitrate nitrogen were designated tentatively as desirable to be maintained under the various crops throughout the growing season:

	p.p.m.
1. Golden Plume celery, lettuce, and late beets.....	10
2. Golden Acre cabbage.....	15
3. Early tomatoes and late spinach.....	20

Nitrate accumulations from the oats, rye, and timothy green manures were correlated positively with the percentages of nitrogen in the crop decomposed, but the differences were obscured by the fertilizer nitrogen applied before a succeeding crop of celery.

Oats green manure was increasingly detrimental to celery as the percentages of nitrogen in the oats crops compared were greater, but the injury could not be ascribed to the accumulation of nitrates from the decomposition of the crop.

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SOME FACTORS INVOLVED IN STUDYING THE FIXATION OF PHOSPHORUS BY SOILS¹

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The fixation phenomenon of soils is by no means new to soil investigators, although, like many other phenomena, there are, no doubt, many things yet to be learned about it. As early as 1850 Way (14) expressed very definite ideas concerning the fixation of various substances by soils. Fixation may be either chemical or physical and is usually referred to as "absorption." There is another term "adsorption" which is sometimes used although there is a feeling on the part of some investigators that this term might well be dropped. In this work the writer has chosen to dispense with both of the aforementioned terms and to use only the term "fixation."

The power which soils have of fixing substances from solution is a very important factor in soil fertility. Applied fertilizers as well as plant-food materials dissolved from the soil particles are prevented, through the phenomenon of fixation, from being lost by leaching, while at the same time they are fairly accessible to the plant. As a rule when salts, the anions of which form soluble compounds with soil cations, are applied to soils the cations become fixed while the anions are free to leach out or unite with other bases that have been liberated. This is not true, however, in the case of a phosphorus salt that is applied to a soil, for the phosphate radical is itself fixed.

The object of this work is not to determine whether phosphorus is fixed by the soil but rather to point out some of the things that must be considered in studying the fixation of phosphorus by soils.

A search of the literature reveals the fact that considerable attention has been given by soils investigators to the fixation phenomenon. There seems to be considerable difference of opinion as to whether it is a chemical or a physical phenomenon. Researches seem to indicate that there can be either chemical or physical fixation. Occasional reference is made in the literature to the term "negative fixation." This, in the writer's opinion, is not true negative

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fixation but merely a case of a soil being unable to fix as much of a substance as was contained in the water that was rendered unfree or taken out of the rôle of a solvent by the soil. In such case the excess of substance goes to concentrate the remaining free solution, making it seem as if some of the substance in question had actually been dissolved from the soil.

EXPERIMENTAL WORK

In some preliminary work in which muck soils were treated with a 0.1*N* solution of $\text{CaH}_4(\text{PO}_4)_2$ and the supernatant liquid was analyzed, it appeared that approximately six times as much phosphorus was fixed as when the same soils were treated with a 0.02*N* solution of the same salt. It is evident that if a more dilute solution had been used there would have been indications of a still smaller amount of phosphorus fixed. We might reason further that if a very dilute phosphorus solution were added to a soil containing large quantities of phosphorus the soil would give up some of this element, which would go to concentrate the remaining solution. This would be an example of the writer's idea of true negative fixation. It was also found (8) that when either 0.1*N* or 0.033*N* solutions of KCl were kept in contact with muck soils for a period of about 16 hours the solutions became less concentrated with potassium than they were before being added to the soil, whereas a normal solution of the same salt kept in contact with the same soil for the same length of time was found to be more concentrated than it was before being added to the soil. The latter is a case of what is commonly called "negative absorption," but which is, in reality, a case of the soil being unable to hold as much potassium as was contained in the water fixed by the soil.

With these thoughts in mind the writer attempted to find out, if possible, more about the phenomenon of the fixation of phosphorus, especially by muck soils. Four samples of muck were chosen with care from as many different muck deposits in the vicinity of the college. These deposits have become fairly well known by the following names, which will be used throughout this paper:

1. Woodworth muck, which is well drained and supports vegetation although it is quite acid.
2. Trowbridge muck, which is very poorly drained and exceedingly acid—too acid, in fact, to support plant growth.
3. Town Line muck, which is fairly well drained and underlain with marl at a shallow depth, although it has a pH value of less than 7.
4. College muck, which is fairly well drained and only slightly acid in reaction. All of these samples were taken from the surface 6 inches. They were brought from the deposits, sifted through a $\frac{1}{16}$ -inch mesh sieve, air-dried, and thoroughly mixed.

In studying the fixation of phosphorus by these mucks the following method, which is very similar to that used by other investigators, was adopted: Five grams of the air-dried material was placed in Erlenmeyer flasks in duplicate and 50 cc. of the desired phosphorus solution added. The flasks were stoppered,

TABLE I
Phosphorus fixed by four different mucks treated with phosphorus solutions of different concentrations

TROWBRIDGE				WOODWORTH				TOWN LINE				COLLEGE FARM			
P added	P recovered	P fixed	mgm.	P added	P recovered	P fixed	mgm.	P added	P recovered	P fixed	mgm.	P added	P recovered	P fixed	mgm.
109.27	104.55	+4.72*	mgm.	109.27	91.05	+18.22	109.94	78.24	+31.70	109.27	97.79	+11.48	mgm.	mgm.	
211.10	208.40	+2.80	211.11	188.20	+22.91	214.15	168.62	+45.53	211.25	186.82	+24.43				
313.00	308.90	+4.10	313.00	204.70	+18.30	318.35	266.42	+51.93	313.22	288.00	+25.22				
414.80	418.80	-4.00†	414.80	402.00	+12.80	422.60	371.00	+51.60	414.94	383.78	+31.16				
516.60	511.90	+4.70	516.60	503.20	+13.40	526.80	470.10	+56.70	517.31	481.58	+35.73				
614.80	616.45	-1.65	614.80	609.10	+5.70	633.80	574.00	+59.80	620.64	590.80	+29.84				
713.05	720.30	-7.25	713.10	709.60	+3.50	740.70	585.30	+55.40	723.98	691.30	+32.68				
811.20	820.80	-9.60	811.20	814.70	-3.50	847.70	779.00	+68.70	827.25	792.50	+34.75				
909.40	926.00	-16.90	909.40	923.30	-13.90	954.70	886.30	+68.40	930.60	898.40	+32.20				
1,007.60	1,021.80	-14.20	1,007.60	1,035.30	-27.70	1,061.70	991.50	+70.20	1,033.95	1,013.10	+20.85				
Original pH value	3.21			3.70				5.63				5.51			

* + signs indicate positive fixation.

† - signs indicate that the final solution was more concentrated than the original—commonly called “negative fixation” or “negative absorption.”

shaken, and allowed to stand for 24 hours, after which the liquid was filtered off and a phosphorus determination made on an aliquot part of the filtrate. At the same time a phosphorus determination was made on the original solution. It was found that on passing a 0.1*N* solution of $\text{CaH}_4(\text{PO}_4)_2$ through a filter paper no change in phosphorus content could be detected by analysis, although Hardin and Zirban (7) found that a sugar solution was made more concentrated by passing it through a dry filter paper, and less concentrated by passing it through a wet filter paper. To eliminate the possibility of changes in concentrations due to passing the solutions through filter papers, the first few cubic centimeters of filtrate in each case were discarded. The phosphorus determinations were made by the usual volumetric method.

Fixation of phosphorus from solutions of different concentrations

One of the objects of this study was to learn the effect on fixation of adding solutions of different concentrations. In making up these solutions a stock solution was first prepared by adding $\text{CaH}_4(\text{PO}_4)_2$ to water at the rate of 84 gm. per liter. The salt did not all dissolve. The residue was filtered off and from the filtrate a series of dilutions was made by use of carefully calibrated pipettes. The soils were treated in duplicate, as already described, with the aforementioned solutions. After the soil was filtered out it was found necessary to dilute the filtrate further before it was analyzed. This also was done with carefully calibrated pipettes. The results of the analyses, calculated on the basis of the total volumes of solutions added, together with the pH values of the original mucks, are shown in table 1.

The results of the analyses are the averages of two determinations which, in most cases, checked very well.

These figures indicate that the two mucks which were described as being very acid both showed so-called negative fixation of phosphorus from the more concentrated solutions, whereas the other two showed indications of positive fixation from all concentrations of solution used. The writer does not doubt that more phosphorus was fixed from the more concentrated solutions by all four soils than from the more dilute solutions, but two of the mucks indicated negative fixation because they could not fix as much phosphorus as there was in the water that was rendered unfree; hence some phosphorus was left to concentrate the remaining solution. In the case of the other two mucks the phosphorus chemically combined with calcium, which accounts for the great quantity fixed, thus leaving the final solution somewhat diluted. These statements will be substantiated by work reported in this paper.

Fixation of phosphorus by acid mucks treated with lime

Inasmuch as the two mucks with the high pH value showed no negative fixation and the two very acid ones did show negative fixation, the next step was to study the effect of added lime on the fixation of phosphorus by the very sour mucks. Eleven 100-gm. samples were weighed out of each batch of very sour

muck and mixed thoroughly with varying quantities of calcium oxide. The following treatments were made per acre, considering an acre 6 inches of muck soil to weigh 1,000,000 pounds: no treatment, 1 ton, 3 tons, 5 tons, 7 tons, 9 tons, 11 tons, 13 tons, 16 tons, 20 tons, and 25 tons. These quantities of calcium oxide were weighed out and mixed thoroughly in a mortar with a small portion of the muck sample and then added to the remainder and mixed thoroughly with it. This provided for a uniform distribution of the calcium oxide throughout the muck. Ordinarily the oxide tends to remain in little balls and does not mix thoroughly with the soil. When these mixtures were made they were placed in jars and 1 liter of water was added to each. They were shaken occasionally for a week and then filtered and dried, after which fixation studies were made on them. The check sample was treated with water in the same way as the rest but it received no calcium oxide. In making these

TABLE 2
Phosphorus fixed by Trowbridge and Woodworth muck treated with calcium oxide

CaO TREATMENT	TROWBRIDGE			WOODWORTH		
	P added	P recovered	P fixed	P added	P recovered	P fixed
tons	mgm.	mgm.	mgm.	mgm.	mgm.	mgm.
None	636.10	640.10	-4.00	657.60	648.80	8.80
1	636.10	639.40	3.30	657.60	645.50	12.10
3	636.10	534.00	2.10	657.60	538.10	19.50
5	636.10	631.30	4.80	657.60	627.30	30.30
7	636.10	629.30	6.80	657.60	629.30	28.30
9	636.10	627.25	8.85	657.60	623.20	34.40
11	636.10	619.85	16.25	657.60	621.90	35.70
13	636.10	613.75	22.35	657.60	599.60	58.00
16	636.10	586.10	50.00	657.60	573.30	84.30
20	636.10	551.70	84.40	657.60	540.30	117.30
25	636.10	508.50	127.60	657.60	505.90	151.70

studies the concentrations of phosphorus that gave approximately no fixation when added to the untreated muck were used. The results of these treatments are shown in table 2.

In preparing the phosphorus solutions with which to treat these soils, concentrations that would give exactly zero fixations were not secured. They were near enough the right concentrations, however, to serve the purpose very well. We see that by adding to 5 gm. of the Trowbridge muck 50 cc. of solution containing 636.1 mgm. of phosphorus there was a negative fixation of 4.0 mgm. If several samples of this muck, not treated with CaO, had received the same treatment of phosphorus solution, the fixation in each case would have been the same, but when the muck receiving 25 tons of CaO was subsequently treated with the aforementioned phosphorus solution it fixed 127.5 mgm. of phosphorus. This difference in the amount of phosphorus fixed was due to

the calcium present. The increase in phosphorus fixation due to the presence of lime was not directly proportional to the magnitude of the lime treatment. The figures in table 2 show that there was a slight increase in fixation with the increase in lime treatment up to a certain point and from there on the increase in fixation was much greater than the increase in amount of lime added. Such variations are, in all probability, due to the formation of different compounds of phosphorus and calcium. The same results in general hold true with the Woodworth muck. It is interesting to note at this time that the 25 tons of CaO per 1,000,000 pounds of muck did not neutralize the Trowbridge muck and it raised the pH value of the Woodworth muck only slightly above 7. That gives one an idea of the extreme acidity of these materials.

TABLE 3

Phosphorus fixed by town line muck treated with HCl and with KCl and subsequently treated with phosphorus solutions of different concentrations

HCl			KCl		
P added mgm.	P recovered mgm.	P fixed mgm.	P added mgm.	P recovered mgm.	P fixed mgm.
104.14	81.61	22.53	106.60	85.00	21.60
206.39	174.69	31.70	210.40	170.60	39.80
308.64	275.19	33.45	314.30	263.00	51.30
410.90	370.30	40.60	418.20	362.20	56.00
513.28	475.50	37.78	522.00	462.70	59.30
615.00	575.30	39.70	625.90	561.20	64.70
717.00	685.95	31.05	729.80	669.10	60.70
818.40	785.75	32.65	833.60	769.60	60.70
920.60	888.30	32.30	937.50	874.80	62.70
1,022.30	996.90	25.40	1,041.40	980.70	60.70

Fixation of phosphorus by high lime mucks after treatment with KCl and HCl

Since fixation of phosphorus could be so markedly increased in sour mucks by the addition of lime, it was thought well to study the effect on the fixation of phosphorus by high lime mucks by removing the lime with acid or by substituting for calcium a base that forms a more soluble compound with phosphorus. Accordingly two 200-gm. samples of the Town Line muck were weighed into jars. To one was added 1 liter of 3*N* KCl and to the other was added 1 liter of 0.1*N* HCl. The mucks were allowed to remain in contact with these solutions for 24 hours and then they were thrown on filter papers in large funnels and allowed to drain. The necks of the funnels were then stoppered and another liter of solution was added to each one. These solutions were allowed to drain off at the end of 24 hours and each sample was washed with 3 liters of water. The 3*N* solution of KCl was recommended by Gedroiz (5)

for substitution of bases in mineral soils. He reports that the major portion of the calcium is usually removed from mineral soils by the first few leachings. Gedroiz also used 10 per cent HCl solution for removing bases from mineral soils. It was thought that a 10 per cent solution of HCl would be too strong to add to an organic soil; hence the weaker solution was used. The washing was perhaps insufficient to remove the excess HCl and KCl from these materials. Further washing was avoided, however, because washing removed a large amount of the colloidal portion of the organic material, especially when treated with KCl. In this case the leachings were almost black with organic colloids. The fixation studies were made on these soils by the method already described. The results are shown in table 3.

The treatment of this muck with KCl solution increased its alkalinity considerably, which is in accord with the findings of other investigators, but the figures do not show that it decreased, to any extent, its power to fix phosphorus. The HCl treatment, however, did cause a considerable decrease in phosphorus fixation although there was no negative fixation manifested. Had this muck been treated with a stronger solution of HCl it is quite likely that it would have shown negative fixation of phosphorus from a concentrated solution. The writer has found (unpublished data) that when high lime mucks were treated with HCl solutions of different concentrations before the phosphorus fixation studies were made, the samples which received more concentrated solutions of HCl fixed correspondingly smaller quantities of phosphorus.

Fixation of phosphorus by mucks after addition of as much water as they will hold unfree

We have seen that very acid mucks seem to fix phosphorus negatively from concentrated solutions; that high lime mucks do not fix phosphorus negatively from solutions of any concentrations; that very acid mucks, when treated with lime, do not fix phosphorus negatively; and that high lime mucks tend to fix less phosphorus from concentrated solutions after they are treated with acid. It remains now to show an explanation for the so-called negative fixation of phosphorus, which the writer believes to be due to the irregular ratio between the amounts of phosphorus and water fixed from solutions of different concentrations.

The amount of unfree water which these mucks would hold was determined by use of the dilatometer method devised by Bouyoucos (2), and this amount of distilled water was added to the muck samples before the phosphorus fixation studies were made on them. Although the figures obtained by the use of the dilatometer method for determining unfree water may not represent the exact amount of water that the mucks will take out of the rôle of a solvent they will serve very well in the attempt to show the cause of so-called negative fixation.

For this work samples of Trowbridge muck and Woodworth muck were weighed into Erlenmeyer flasks as already explained, and as much water was

added to each sample as it would hold unfree. The samples were then treated with phosphorus solutions of different concentrations and the fixation determinations made as already explained. The results of this work are shown in table 4.

The 1 cc. of water added to 5 gm. of air-dried Trowbridge muck was sufficient with the water already in it to make 28 per cent. Likewise the 1.4 cc. added to Woodworth muck was sufficient to make 38 per cent. Table 4 shows that when as much water is added to a muck as it will hold unfree there is not much variation in the amount of phosphorus that the muck will fix from solutions of different concentrations. In contrast to the results obtained as shown in table 1, there is no indication of negative fixation in such cases when these same mucks are treated with phosphorus solutions of different concentrations without first adding as much water as they would hold unfree.

TABLE 4

Phosphorus fixed by very acid mucks with as much pure water added as they would hold unfree

TROWBRIDGE MUCK, 5 GM. PLUS 1.0 CC. PURE WATER			WOODWORTH MUCK, 5 GM. PLUS 1.4 CC. PURE WATER		
P added mgm.	P recovered mgm.	P fixed mgm.	P added mgm.	P recovered mgm.	P fixed mgm.
105.62	94.41	11.21	103.06	87.68	15.38
209.09	190.20	18.89	206.39	183.46	22.93
312.54	302.16	10.38	309.86	286.00	23.86
415.00	408.73	7.27	413.05	389.85	23.20
519.17	515.30	3.87	516.63	492.35	24.28
624.65	615.76	8.89	619.82	592.19	27.63
730.00	720.32	9.68	723.00	698.75	24.25
835.35	824.14	11.21	826.20	793.20	33.00
940.80	930.72	10.08	929.38	903.80	25.58
1,046.20	1,035.30	10.10	1,032.70	1,009.00	23.70

It is evident, judging from the results of this work, that if there were some method for determining accurately the amount of water that a soil will remove from the rôle of a solvent it would be more nearly possible to determine the exact amount of material that the soil will fix from solution.

SUMMARY

1. Phosphorus fixation studies were made on two very acid mucks and on two more nearly neutral mucks by treating them with solutions of $\text{CaH}_4(\text{PO}_4)_2$ of different concentrations.
2. These studies were repeated on one of the latter after one sample was treated with KCl and one with HCl .
3. Phosphorus fixation studies were made on the two very acid mucks by treating them with phosphorus solutions of uniform concentration after they had been treated with varying amounts of calcium oxide.

4. Phosphorus fixation studies were made on the two very acid mucks after as much distilled water had been added as they would hold unfree.

CONCLUSIONS

1. Very acid mucks show indications of negative fixation of phosphorus when treated with a highly concentrated solution of $\text{CaH}_4(\text{PO}_4)_2$. This phenomenon is due to the fact that the mucks can not fix as much phosphorus from a concentrated solution as there is in the water that is rendered unfree, and some of this phosphorus is liberated and goes to concentrate the remaining solution.

2. Mucks with a relatively high pH value do not show any indications of negative fixation of phosphorus regardless of the concentration of the solution with which they are treated. This is, no doubt, due to the fact that the phosphorus reacts chemically with the lime to form an insoluble compound.

3. Very acid mucks show no indications of negative fixation of phosphorus from solutions of any concentration, provided they are treated with lime before the fixation studies are made. In this case again the phosphorus reacts with the lime to form an insoluble compound.

4. When high lime mucks are treated with acid their ability to fix phosphorus from solution is considerably lessened.

5. When mucks that show an indication of negative fixation are treated with as much water as they can render unfree the phosphorus fixation results will be positive regardless of the concentration of the phosphorus solution with which they are treated.

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FERTILIZER STUDIES WITH SWEET POTATOES¹

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On account of the special growth requirements of the sweet potato plant, the production of this crop has been very largely confined to the Southern States. In Georgia, North Carolina, Alabama, and Mississippi, the growing of sweet potatoes constitutes an important agricultural enterprise. The crop is also grown to a considerable extent in certain sections of Maryland, Delaware, Virginia, and southern New Jersey where climate and soil conditions are both particularly suitable. In these states, moderate applications of commercial fertilizer are generally used for sweet potato production, but in some instances as high as 800 to 1000 pounds of fertilizer are applied per acre. Consequently, fertilizer problems, involving the use of organic and inorganic nitrogenous materials, and different forms of potash, are of especial importance in these cases particularly.

The present experimental work was conducted for the purpose of studying the relative effects of fertilizers containing different amounts of nitrogen and potassium materials on the yield and growth of sweet potatoes. In addition, an experiment on the effectiveness of increasing the rate of fertilizer application was also included in the present work.

REVIEW OF LITERATURE

It is significant that a large portion of the experimental work on fertilizers for sweet potatoes has been concerned chiefly with the effects produced by nitrogen and potassium. That these two elements are important in sweet potato production was brought out rather strikingly by Keitt (5) in a chemical analysis of fourteen different varieties of sweet potatoes. His results showed that the following amounts of nitrogen, phosphoric acid, and potash were removed from the soil by the sweet potato storage roots:

	<i>per cent</i>
Nitrogen.....	0.348 -0.184
Phosphoric Acid.....	0.0893-0.0435
Potash.....	0.684 -0.336

It would seem from these results that nitrogen and potash should be expected to play a more important part than phosphorus, in the fertilization of sweet potatoes. Consequently, various nitrogen and potassium materials have been used more than phosphorus materials for fertilizer studies with sweet potatoes. Scott (10) found, as a result of five years' study on fertilizers for sweet potatoes, that both sulfate of ammonia and dried blood were suitable

¹ Part II of a thesis submitted to the graduate faculty of the University of Maryland, June, 1928, in partial fulfillment of the requirements for the degree of doctor of philosophy.

sources of nitrogen for this crop. He also found that fertilizers containing potash were needed in order to produce a satisfactory yield of potatoes. From a comparison of muriate and sulfate of potash he found that the muriate plot out-yielded the sulfate plot by 18.2 bushels of potatoes. It is rather significant that there were no differences noted in the extent of vine growth on any of the plots.

Stuckey (12), summarized the results of 12 years' experimental work on a comparison of single applications of mineral fertilizer materials, and a complete fertilizer mixture for sweet potatoes. With respect to the yields of potatoes obtained, the fertilizer treatments may be ranked as follows: first, complete; second, sulfate of potash; third, acid phosphate; fourth, nitrate of soda; and fifth, check (no fertilizer). It was stated that yields of potatoes obtained from the various treatments, in comparison with those obtained from the check plots, did not warrant the use of fertilizers in large amounts.

In an earlier publication, Stuckey (11) reported the results of some extensive studies on the effects of different fertilizer materials on the weight and chemical composition of the sweet potato vines produced. It was concluded that high nitrogen applications had a tendency to increase the weight of vines but did not materially affect their chemical composition. Chemical determinations made on the potatoes also showed no significant variations for the different treatments. Nitrate of soda used alone produced the smallest potatoes, whereas a complete fertilizer and likewise a sulfate of potash treatment, had a tendency to increase the size. Neither the percentage of starch nor the percentage of sugar showed significant differences in the potatoes produced, where a 2-12-2 and where a 3-12-4 fertilizer was applied each year over a period of two years. It was concluded from a comparison of the weight of vines produced and the yield of potatoes, that the size of the crop cannot be forecast from the extent of the vine growth.

Contrary to the results obtained by Stuckey (11), it is commonly thought that there is a relation between the growth of sweet potato vines and the yield of sweet potatoes. For lack of experimental evidence, much doubt exists concerning the effect of various fertilizer materials, on the production of sweet potato vines and storage roots. However, more is known about the effect of fertilizer materials on the shape of sweet potatoes. Results of field experiments have been obtained which indicate that certain fertilizer ingredients tend to produce long narrow sweet potatoes and others tend to produce short thick ones. Whether this effect is directly associated with the manufacture and translocation of carbohydrate materials for root storage, or merely the resultant of a change in the relationship between vine growth and root storage is not known. In respect to the effects of fertilizers on the shape of sweet potatoes, the work of Schermerhorn (9) is of particular interest. He found that increasing amounts of nitrogen in the fertilizer mixture produced a relatively long potato; whereas increasing amounts of potash produced a potato of the "chunk" type. These results are particularly significant from an economic standpoint, since the market at the present time demands a "chunk" type of sweet potato. The same author obtained increased yields of potatoes when complete fertilizers containing as high as 8 per cent potash were used. A complete fertilizer containing this amount of potash produced an increased yield of 99.5 bushels of potatoes over that obtained from the no-potash treatment.

Several attempts have been made to determine the relation between the starch and sugar content of the sweet potatoes and the kind of fertilizer used, but the results so far have been unsatisfactory. However, Quinn (8), in 1925, found a definite correlation between the amount of potash used as fertilizer and the percentage of carbohydrates in the potatoes produced. It was claimed that potash applications not only increased the percentage of starch and sugars, but also produced a larger yield of marketable potatoes. It is interesting to note that Quinn also observed that the vine growth was unaffected by the fertilizer treatments.

Johnson, Zimmerly, and Geise (4) studied the relative effects of several sodium and potassium salts, when used for top-dressing sweet potatoes. It was found that the complete fertilizer plots which were top-dressed with sodium chloride produced an average increase of 42.7 bushels of marketable potatoes over the yield obtained from the same treatment without

the sodium chloride top-dressing. This increase was consistent for both the late and early harvest of the sweet potatoes. It was pointed out that all of the treatments containing chloride salts compared very favorably with those containing sulfates.

As a result of several years' experimental work, chiefly with single applications of fertilizer materials, Geise (1) concluded that a complete fertilizer was essential for the production of sweet potatoes. However, he found that responses in yields from potassium applications were, as a rule, greater than the responses from nitrogen or phosphoric acid applications. The results of an experiment for one year showed an increase of 40 bushels of potatoes from a 2-8-10 fertilizer treatment, over the yield obtained from a 2-8-8 treatment. Likewise, a 3-8-10 fertilizer treatment outyielded a 3-8-8 treatment by 23 bushels of potatoes.

As strong as the case may seem for the beneficial effects of potash treatments on sweet potatoes, results have been reported where potash applications have not produced increased yields. Hotchkiss (2) found, from a comparison of several fertilizer materials used alone and in different combinations, that sulfate of potash gave the lowest yield of any treatment. It was pointed out that apparently potash was not a limiting factor in the soil used for the experiments. Knapp (6) also reported no increases in yields of sweet potatoes where potash applications were made.

From the foregoing review of literature it seems quite evident that potash and nitrogen in some form are needed for sweet potato production on the majority of soils. Exactly which form of nitrogen and potash is best is still a matter to be determined by experiment, probably for each soil condition.

GENERAL PLAN OF EXPERIMENTS

The present fertilizer experiments with sweet potatoes constituted part of an extensive series of fertilizer experiments with early potatoes conducted at Snow Hill, Maryland. These experiments were started in 1924 but the yields for this year were not reported on account of a crop failure.² Throughout the work, the sweet potato plots were used as part of a two-year rotation with early potatoes. The results of the early potato work were reported in an earlier publication (3).

A complete description of the soil conditions in the vicinity of Snow Hill is given in an earlier publication (3), so that it will be sufficient to state here that the topography is extremely flat with an occasional sand hill typical of the Coastal Plain region.

Nearly three acres were used for experiments with fertilizers on sweet potatoes, the remaining three acres being used for similar experiments with early potatoes. The soil, mapped as Norfolk sandy loam, is characteristically low in nitrogen, phosphorus, and potash. Because of its sandy nature, it is also subjected to considerable leaching during the wet months of summer and winter. The amount of rainfall for the sweet potato growing season of each year, as taken from the records made at Public Landing, Maryland, seven miles from the experimental field was as follows: 1925, 11.18 inches; 1926, 24.42 inches; 1927, 19.41 inches.

Plots $\frac{1}{10}$ and $\frac{1}{40}$ acre in size were used, and these were so arranged as to

² The yields for 1925 were obtained by Dr. A. M. Smith.

allow for the continued application of the same fertilizer materials on each plot year after year. Only the rate and analysis of fertilizer varied each year. Such an arrangement was made in order to study the residual effects of the fertilizers applied. Rye and vetch were seeded after the potatoes were dug and served as a green manure cover crop on the land until the following spring. In one series the land was left bare, in order to make a comparative study of green manuring on yields.

The fertilizer treatments were applied in the row with a one-row fertilizer distributor about May 20-23 of each year, and the sweet potato sprouts were transplanted as soon after this as possible. Locally grown sprouts of the Big Stem Jersey variety of sweet potato were planted, a transplanting machine being used whenever possible. It should be noted particularly that the entire amount of all the fertilizer treatments was applied before the sprouts were transplanted.

Harvesting operations were usually commenced about October 10, depending upon the season and the market conditions. The potatoes were plowed up and later scratched out by hand in the manner customary in the locality. All grading was done in the field using three grades, U. S. Grade No. 1—primes, culls, and strings. The weights of primes and culls were recorded in the field at harvest, the strings being discarded.

Throughout the entire work discussed in this paper, it should be noted particularly that no single treatments of fertilizer materials were made for comparison, because previous work and local cultural practices indicated that a complete fertilizer was more suitable for the production of satisfactory yields of sweet potatoes. In discussing the present work the results of the different experiments have been arranged in series and numbered consecutively for convenience. The series numbers, therefore, do not correspond in all cases with those used in the field.

Series 1. Influence of different forms of nitrogen in the fertilizer mixture

The purpose of this series was to make a comparative study of certain inorganic and organic nitrogenous materials when used alone and in combinations in the fertilizer mixture. The fertilizer used for each treatment, except for the check plots, was made up to contain the equivalent of 3 per cent ammonia, 8 per cent phosphoric acid, and 8 per cent potash. The phosphoric acid and potash for this series and all subsequent work, unless otherwise stated, were derived from 16 per cent superphosphate and sulfate of potash, respectively. The application was made at the rate of 1000 pounds of fertilizer per acre, in the same manner as previously described. The yields of prime potatoes for 1925, 1926, and 1927, the average yield for the three-year period, and the average yield in bushels per acre, are given in table 1 together with the average percentage of culls for each treatment.

In consideration of the yields of potatoes which were obtained from the different treatments for each year, it is quite evident that the results varied

considerably from year to year. In 1925, undoubtedly, the extreme drought caused a general depression of all the yields, so that moisture and not fertilizer appeared to be the limiting factor during this year. Therefore, the present discussion will be confined to the results obtained during the following two years, 1926 and 1927.

The most important results for 1926 and 1927 were obtained where nitrate of soda, sulfate of ammonia, and urea were used alone as sources of nitrogen in the fertilizer mixture. The yields from these plots, when compared with those obtained from the plots receiving nitrogen only in the organic form, serve to show the importance of soluble mineral nitrogenous compounds in the

TABLE 1
Yield of sweet potatoes from plots treated with varying amounts of different forms of nitrogen in 3-8-8 fertilizer

AMMONIA IN MIXTURE FROM:	YIELD-PRIMES PER ACRE				TOTAL YIELD, AVER- AGE	CULLS, AVER- AGE
	1925	1926	1927	3-year average		
	bu.	bu.	bu.	bu.	bu.	per cent
Nitrate of soda.....	12	245	152	136	184	26.0
Sulfate of ammonia.....	11	184	147	114	142	19.7
Dried ground fish.....	8	170	86	88	142	38.0
0-8-8. No ammonia.....	9	39	76	41	91	54.9
Packing house tankage.....	14	118	81	71	136	47.7
$\frac{1}{2}$ sulfate and $\frac{1}{2}$ nitrate.....	11	168	74	84	138	39.1
$\frac{1}{2}$ fish and $\frac{1}{2}$ tankage.....	16	106	116	80	140	42.8
40 per cent inorganic,* 60 per cent organic†.....	11	155	143	103	166	37.9
50 per cent inorganic, 50 per cent organic.....	25	95	132	84	163	48.4
60 per cent inorganic, 40 per cent organic.....	18	192	107	106	161	34.1
0-8-8. No ammonia.....	46	40	136	74	124	40.3
70 per cent inorganic, 30 per cent organic.....	53	201	43	99	151	34.4
80 per cent inorganic, 20 per cent organic.....	78	120	73	90	157	42.6
Urea.....	5	143	204	117	165	29.0
Activated sewage sludge.....	20	123	148	97	155	37.4

* Inorganic = $\frac{1}{2}$ nitrate of soda and $\frac{1}{2}$ sulfate of ammonia.

† Organic = $\frac{1}{2}$ fish and $\frac{1}{2}$ tankage.

fertilizer mixture for sweet potatoes. An average yield of 136 bushels of potatoes was produced where nitrate of soda was used as a single source of nitrogen, and an average yield of 114 bushels was produced where sulfate of ammonia was similarly used. However, an average yield of only 88 bushels of potatoes was produced with dried ground fish as the only source of nitrogen. A still lower average yield of 71 bushels was obtained where packing house tankage was used. From these results it would seem, that sweet potatoes required a soluble nitrogen material to produce the best yields on this soil. It is possible that the nitrification of the organic materials did not take place rapidly enough to supply a sufficient amount of nitrates during the critical

period of growth soon after the sweet potato sprouts were transplanted. Moreover, it is wholly possible that a supply of nitrates was prolonged throughout the first part of the growing season, in the cases where organic materials were used. The deferred supply of nitrates may have induced late vine growth and thus retarded the processes of carbohydrate storage in the roots. This phase of the problem offers a very fruitful field of research which perhaps may be found closely associated with the work of Kraus (7) and others on the carbon-nitrogen relations in plants, as modified by the supply of nutrients in the soil. Some greenhouse studies with sweet potatoes have already been commenced for the purpose of studying this phase of the problem, but the work has not progressed far enough to give results.

A comparison of the average yields produced where only soluble nitrogen materials were used, shows the highest average yield where nitrate of soda was applied. However, from the standpoint of smoothness and quality, the potatoes produced where urea was used in the mixture were far superior to those produced on any other plot in the series. With respect to the relative mechanical conditions of the mixtures, it is worthy of note that the urea mixture could be drilled without the slightest difficulty, whereas the nitrate of soda and sulfate of ammonia mixtures had to be remilled before they could be drilled.

Of the various treatments containing different percentages of inorganic and organic nitrogen, none seemed to be especially superior. The 60 per cent inorganic and 40 per cent organic ratio, however, gave the highest 3-year average yield of all the combinations. It is evident from table 1 that mineral nitrogenous materials, used alone in the fertilizer mixture, outyielded the treatments containing both inorganic and organic materials. However, conclusions should not be drawn from these results without a consideration of the soil conditions that usually exist where the sweet potato crop is grown. It is a well-known fact that sweet potatoes grow best on loose sandy soils. Naturally, losses of nitrates from such a soil during wet seasons are heavy. For this reason, and also to provide for a better mechanical condition of the mixture, it would seem safer to supply the nitrogen from both organic and inorganic sources. The 60 per cent inorganic and 40 per cent organic ratio appears to be a good combination for this soil.

The percentage of culls produced was perhaps influenced more by seasonal differences than by any other contributing factor. It is significant, however, that on the three plots which produced the lowest average percentages of culls the treatments were nitrate of soda, sulfate of ammonia, and urea, all used alone as sources of nitrogen in the fertilizer mixture (table 1).

Series 2. Comparative effects of certain of the newer nitrogen compounds used in a fertilizer mixture

This series of plots was laid out in 1927 for the purpose of studying the effects on yield of sweet potatoes, when nitrate of soda, sulfate of ammonia,

Leunasalpeter, and urea were used in the fertilizer mixture in various ways. Wherever organic nitrogen was used in this series, it was supplied in equivalent amounts from dried ground fish and packing house tankage. The fertilizer analysis was the same as that used for series 1, a 3-8-8 mixture. The treatment, however, was applied at the rate of 1500 pounds per acre instead of 1000 pounds as was done previously. The entire amount of each fertilizer treatment was applied as usual before the sprouts were transplanted. The yields of primes and of culls and the total yield for the different treatments in 1927 are shown in table 2.

The results given in table 2 indicate that, under the conditions of the experiment, Leunasalpeter plus organics, was a combination as suitable for sweet potatoes, as was nitrate of soda or sulfate of ammonia also used with

TABLE 2

Effects on yield of sweet potatoes when different nitrogenous materials were used in a 3-8-8 fertilizer in 1927

AMMONIA IN MIXTURE FROM:	YIELD POTATOES PER ACRE		
	Primes bu.	Culls bu.	Total bu.
70 per cent nitrate of soda, 30 per cent organic*.	130	15	145
70 per cent sulfate of ammonia, 30 per cent organic.....	146	61	207
70 per cent leunasalpeter, 30 per cent organic....	159	56	215
50 per cent urea, 30 per cent sulfate of ammonia, - 20 per cent organic.....	182	55	237
20 per cent nitrate of soda, 50 per cent sulfate of ammonia, 30 per cent organic.....	171	48	219
Urea.....	146	33	179
Leunasalpeter.....	126	51	177

* Organic = $\frac{1}{2}$ fish and $\frac{1}{2}$ tankage.

organics. The yield of primes produced on the plot treated with Leunasalpeter plus organics, was somewhat higher than that obtained from nitrate of soda, but it was about the same as that produced with sulfate of ammonia. However, when used alone in the mixture, Leunasalpeter produced a yield of primes 20 bushels lower than that which was obtained with urea. Here again, however, the total yields were about the same.

From the results of the various combinations, it would seem that both urea and Leunasalpeter produced better yields when they were used with the organic nitrogenous materials. It is possible that another year's results will show more conclusively how these materials may best be used for sweet potatoes, but it will be necessary to have several years' data, before the effect of variations in seasons can be considered.

Series 3. Effect of a green manure cover crop in addition to a fertilizer application

The question of conserving the portion of the fertilizer not utilized by the sweet potato crop is as important in growing this crop as it is in every case where large amounts of fertilizer are applied to crops grown on sandy soils. To effect this conservation, in the present work the land was disced thoroughly after the sweet potatoes were harvested, and rye and vetch were seeded. For determining the relative effect of green manuring, seven treatments, duplicating certain treatments shown in table 1 and applied in the same manner, were used in series 3 but without a green manure cover crop. By this arrange-

TABLE 3

Effect of green manure cover crop in addition to fertilizer treatment on the yield of sweet potatoes

AMMONIA IN MIXTURE FROM:	YIELD-PRIMES PER ACRE			3-YEAR AVERAGE
	1925	1926	1927	
	bu.	bu.	bu.	bu.
Nitrate of soda.....	37	173	56	89.0
Nitrate of soda plus green manure.....	12	245	152	136.0
Sulfate of ammonia.....	46	157	31	78.0
Sulfate of ammonia plus green manure.....	11	184	147	114.0
Dried ground fish.....	29	148	13	63.0
Dried ground fish plus green manure.....	8	170	186	88.0
40 per cent inorganic,* 60 per cent organic†.....	30	136	48	71.0
40 per cent inorganic, 60 per cent organic plus green manure.....	11	155	143	103.0
50 per cent inorganic, 50 per cent organic.....	30	180	40	83.0
50 per cent inorganic, 50 per cent organic plus green manure.....	25	95	132	84.0
60 per cent inorganic, 40 per cent organic.....	37	156	42	78.0
60 per cent inorganic, 40 per cent organic plus green manure.....	18	192	107	106.0
70 per cent inorganic, 30 per cent organic.....	33	139	57	76.0
70 per cent inorganic, 30 per cent organic plus green manure.....	53	201	43	99.0

* Inorganic = $\frac{1}{2}$ nitrate of soda and $\frac{1}{2}$ sulfate of ammonia.

† Organic = $\frac{1}{2}$ fish and $\frac{1}{2}$ tankage.

ment, a comparison of different fertilizer treatments with and without green manure was made possible. The yields of primes for each treatment for 1925, 1926, and 1927, together with the average yield over the three-year period, are shown in table 3.

In considering the data presented in table 3, it becomes necessary to disregard the yields for 1925, as the dry weather during that season evidently seriously affected the entire sweet potato crop. In 1926, the plots receiving green manure were located on a sandy hill, whereas the no-green manure plots were situated on comparatively level land. As a consequence, the increases

shown for green manure in 1926 are very likely due in part to soil differences. Furthermore, it may be seen from table 3 that better yields were produced on the sandy hill in 1926 than were obtained in 1927 on the level land. In 1927 all plots were located on the level portion of the field, however, and it may be seen from the data, that increases for green manure still persisted. In considering the three-year average yields, it will be noted from table 3, that the relative increases for green manure were greater where nitrate of soda and sulfate of ammonia were used, than where dried ground fish was used. Evidently, the maximum returns were obtained from the soluble nitrogen materials only in conjunction with a sufficient supply of organic matter in the soil, as in the case where green manures were applied each year. Dried ground fish appeared to be an unsuitable material when used alone in the mixture, even when green manures were supplied in addition to the fertilizer treatment.

TABLE 4
Yields of sweet potatoes produced with a 3-8-8 fertilizer applied at different rates

POUNDS 3-8-8 FERTILIZER PER ACRE	YIELD-POTATOES PER ACRE					
	1926		1927		Average 1926-27	
	Primes	Total	Primes	Total	Primes	Total
	<i>bu.</i>	<i>bu.</i>	<i>bu.</i>	<i>bu.</i>	<i>bu.</i>	<i>bu.</i>
No fertilizer.....	19	121	55	88	37	105
500 pounds*.....	86	107	101	145	94	126
750 pounds*.....	119	178	152	201	136	190
1000 pounds*.....	120	166	204	244	162	205
No fertilizer.....	65	133	130	177	98	155
1250 pounds.....	146	202	203	231	175	217
1500 pounds.....	107	163	168	219	138	191

* Indicates average yields of duplicate plots.

For the inorganic-organic combinations, the greatest increases for green manure were obtained with the 40-60 and the 60-40 ratios. The yields obtained for the 50 per cent inorganic and 50 per cent organic nitrogen ratio were about the same where green manure was added as where the land was left bare.

From a comparison of the yields obtained with and without green manure in addition to the fertilizer treatment, it would seem that the use of green manures as a whole produced consistent increases in yields of potatoes.

Series 4. Effect of different rates of fertilizer applications on yield

A fertilizer mixture containing 3 per cent ammonia, 8 per cent phosphoric acid, and 8 per cent potash was used for all treatments in this series. The ammonia was supplied by equivalent amounts of nitrate of soda, sulfate of ammonia, dried ground fish, and packing house tankage. The phosphoric

acid and potash were derived from 16 per cent superphosphate and sulfate of potash, respectively. The fertilizer treatments were applied in the row just before the sweet potato sprouts were transplanted. The yields of primes and the total yields for 1926 and 1927 are shown in table 4, together with the average yields for the two-year period.

It is evident from the data presented in table 4, that from the standpoint of yields of potatoes, the best rate of fertilizer application was between 1000 and 1250 pounds per acre. The gradual increase in yields as the fertilizer application was increased from 500 to 1000 pounds per acre, is strikingly significant. Likewise, the reduction in yield when the application was increased from 1250 to 1500 pounds per acre, is equally significant. Considering the average increases in yields for the 500 and 750 pound applications over the yields from the check plots, it seems very likely that fertilizer applications at these rates would prove unprofitable on this soil. The decreased yield for the 1500-pound application undoubtedly was caused by an injurious effect of a high concentration of fertilizer salts.

Series 5. A comparison of varying amounts of different potassium materials used in the fertilizer mixture

In the spring of 1927, a series consisting of thirty-one $\frac{1}{40}$ -acre plots was laid out in order to study the relative effects of muriate of potash, sulfate of potash, and manure salts (20 per cent) in a complete fertilizer mixture for sweet potatoes. Each potash material was used to supply equivalent quantities of potash amounting to 5, 8, and 10 per cent in a mixture containing 3 per cent ammonia and 8 per cent phosphoric acid. Seventy per cent of the ammonia was derived from equivalent amounts of nitrate of soda and sulfate of ammonia and 30 per cent from equivalent amounts of dried ground fish and packing house tankage. The phosphoric acid was supplied by 16 per cent superphosphate.

The treatments were applied in triplicate, so that soil variations could be minimized. As a further precaution in this respect the triplicate plots were so located in the series as to utilize part of a representative soil area in three portions of the field. Although the field on which the experiment was located was very uniform in all respects, it was thought advisable to provide several replicate plots for each treatment for the purpose of obtaining material for certain physiological studies that will be carried on from time to time during the progress of the work. Four check plots were provided, each receiving a 3-8-0 fertilizer application.

The plots were managed in the same manner as in the preceding series, except that the fertilizer was applied at the rate of 1500 pounds in each case. A green manure cover crop of rye and vetch was seeded, as usual, when the sweet potatoes had been dug. In table 5 are shown the average yields of primes, culls, and the total yield for the triplicate treatments in bushels per acre, together with the average yield of the four check plots for 1927.

The data presented in table 5 show rather definitely, at least for one year's results, that additions of potash to this soil increased the average yield of sweet potatoes. However, table 5 shows no uniform response from all the potash materials used. Equivalent amounts of potash supplied by manure salts, in every case, produced a lower average yield of prime potatoes than did either muriate or sulfate of potash. Furthermore, it is significant that there were no uniform increases in average yields for the 10 per cent potash applications, over the 5 and 8 per cent potash treatments. Sulfate of potash produced the largest average yield of prime potatoes where the 8 per cent potash mixture was used, but muriate of potash produced the largest yield from the 5 per cent potash mixture. In the case of manure salts, it is probable that the total salt content was high enough to retard the early growth of the young sweet potato sprouts to some extent. On the other hand, it is entirely probable that the large quantity of sodium chloride which was applied with the manure salts

TABLE 5

Yield of sweet potatoes obtained with various potash materials used in different amounts in the fertilizer mixture in 1927

Average yields per acre of triplicate plots

POTASH IN MIXTURE FROM:	3-8-5			3-8-8			3-8-10		
	Primes	Culls	Total	Primes	Culls	Total	Primes	Culls	Total
	bu.	bu.	bu.	bu.	bu.	bu.	bu.	bu.	bu.
Manure salts (20 per cent).....	129	67	196	103	53	156	126	52	178
Muriate of potash.....	167	45	212	109	44	153	134	68	202
Sulfate of potash.....	157	48	205	174	59	233	151	63	214
No potash 3-8-0*.....	99	65	164

* Average yields of four check plots.

may have retarded the nitrification of the organic materials contained in the fertilizer mixture. This toxic action, although probably not capable of stopping nitrification entirely, may have prolonged the supply of nitrates into the growing season, so that there was a tendency for vine growth to occur at a time when the plant would normally be producing carbohydrates for root storage. The toxic effect of large amounts of sodium chloride on nitrification is well known and will be discussed in a later paper in connection with the use of manure salts in fertilizers for potatoes.

From the first year's results for the comparative effects of various potash materials with sweet potatoes, it appears that sulfate of potash was slightly superior to muriate of potash. Whether the increased yields produced from the use of sulfate of potash will justify the additional cost of this material, is a matter that will probably be brought out as the experiment continues. It appeared that manure salts, when compared on an equivalent basis with

muriate or sulfate of potash, were not as suitable as either of the potash materials when used for sweet potatoes on this soil.

Series 6. Effect of double strength fertilizers applied at half rate

Experience has shown that the period shortly after the sweet potato sprout is transplanted is a critical stage in its development. At this time it is possible seriously to retard the growth of the plant by improper application of fertilizers so that the stand will be scattered and a poor yield of potatoes result. With the introduction of highly concentrated fertilizers, the question arose as to their effect when used for sweet potato production. In order to obtain some experimental information in this regard, two treatments of high analysis fertilizers were each applied to $\frac{1}{10}$ -acre plots. These plots were situated close to those in series 2 so that comparisons could be made with the usual fertilizer treatments. One of the fertilizer mixtures was made up to contain 6 per cent ammonia, 16 per cent phosphoric acid, and 16 per cent potash—a double 3-8-8 mixture. The other mixture contained the same amounts of

TABLE 6
Yield of sweet potatoes produced where concentrated mixtures were used in 1927

ANALYSIS	RATE PER ACRE	YIELD POTATOES PER ACRE		
		Primes	Culls	Total
	<i>pounds</i>	<i>bushels</i>	<i>bushels</i>	<i>bushels</i>
6-16-16	750	163	70	233
6- 8-16	750	147	67	214
3- 8- 8	1500	146	33	179

ammonia and potash but only half the amount of phosphoric acid. All the ammonia in the mixtures was derived from urea, the phosphoric acid from 20 per cent superphosphate, and the potash from sulfate of potash. Both mixtures were applied at the rate of 750 pounds per acre before the sprouts were transplanted. The yields of primes and of culls and the total yields expressed in bushels per acre for each treatment, are given in table 6.

It appears from the yields given in table 6 that no harmful effect was produced when the concentrated mixtures were applied at the rate of 750 pounds per acre. These yields compared very favorably with those produced where a 3-8-8 mixture, made from similar materials, was applied at 1500 pounds per acre. It will be noted from table 6 that the yield of potatoes was not appreciably reduced when the usual quantity of phosphoric acid was reduced to half that amount. This result, and those obtained in the foregoing studies, indicate that phosphoric acid is not as essential in the production of sweet potatoes as are nitrogen and potassium.

Although no harmful effects were noticeable where concentrated mixtures were used in 1927, it is possible that different results may be obtained during a

season of lower rainfall. For this reason, it seems advisable to have the results for several seasons before more definite conclusions can be drawn with respect to the use of concentrated mixtures.

SUMMARY OF RESULTS

From a comparison of different forms of nitrogen in a 3-8-8 fertilizer used for sweet potatoes, the soluble materials such as urea, nitrate of soda, and sulfate of ammonia produced the highest average yields of prime potatoes. Of the inorganic-organic combinations the 60 per cent—40 per cent ratio gave the highest average yield of prime potatoes. It was suggested that a soluble nitrogen material in the fertilizer mixture helped to establish the sweet potato sprout in the field.

The results on one year's work with Leunaspelter indicated that it was a very suitable nitrogen material for sweet potatoes, when used in conjunction with organics. In this respect, it compared very favorably with nitrate of soda and sulfate of ammonia.

A green manure cover crop of rye and vetch used in the rotation in conjunction with the regular fertilizer application, gave significant increases in yields of potatoes.

The yields of prime potatoes were larger in every case where potash was used, as compared with the yields obtained where treatments were applied containing no potash. The increases for all the potash materials used were not uniform. Sulfate of potash gave the highest yields, followed by muriate of potash and manure salts, in the order named.

No injurious effects were noticeable when a double strength fertilizer was applied at the rate of 750 pounds per acre for sweet potatoes. It was suggested, however, that a dry season may bring about very different results with concentrated fertilizer mixtures.

CONCLUSIONS

1. Sweet potato fertilizers for Norfolk sandy loam should contain a larger percentage of nitrogen from soluble materials than from the more slowly soluble organic materials.
2. From the standpoint of increased yields of sweet potatoes, it is advisable to use a green manure cover crop in the rotation, especially when large amounts of fertilizer are applied to this soil.
3. From the first year's results with potash materials, sulfate of potash appeared to be a more suitable material in a complete fertilizer mixture for sweet potatoes than did either muriate of potash or manure salts.

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WATER RELATIONS OF PINEAPPLE PLANTS¹

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There is a rather general opinion among Hawaiian pineapple growers, doubtless based on many observations, that pineapple plants are almost as hardy under severe drought conditions as cactus plants. As it is not uncommon to find, under some of the most arid conditions of the Hawaiian Islands, that only cactus, pineapples, and certain other species of plants are able to survive, this opinion of pineapple growers is not very far from the truth.

In the present investigations an attempt is being made to elucidate some of the factors involved in the phenomenon of drought resistance of pineapple plants. Is it a question of: first, an unusually high absorbing power of the roots; second, a low water requirement of the tissues for normal functioning and growth; third, a low evaporation and transpiration rate of the tissues, or fourth, a combination of these and other factors? This question deserves some consideration from an economic point of view. The decision whether or not it would be wise to plant many arid areas to pineapples could be made more intelligently if definite information on the water requirements of pineapple were available.

METHODS OF EXPERIMENTATION

As it is almost impossible, because of the influence of various environmental factors, to maintain a constant moisture content in a soil that has not been placed under absolute control, the results reported in the following pages are only approximate. Absolute control of the environmental factors has never been attempted because of its unnaturalness and the bad effects produced on plants.

The planting material employed for these studies consisted of slips. They were stripped, exposed to sunlight for a week, weighed, and then planted. The soil and plants were placed in 4-gallon heavily glazed stoneware jars, which had previously been air-dried and weighed, and the surface areas of their openings or mouths determined. The soils to be used were air-dried for a week until an approximately constant weight had been reached. The moisture

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in the air-dry soil, i.e. the hygroscopic moisture, was then determined by drying over H_2SO_4 (1.7 sp. gr.) for 24 hours. The same weight of soil—15.0 kgm.—was used for every jar. The amount of water that each soil received was in proportion to its weight, expressed in percentage values, and not in proportion to its water-holding capacity. No drainage was provided with any one of the jars, so that the resulting loss of water can be safely attributed either to evaporation through the top of the jar or to both transpiration and evaporation in those of the jars that contained both plants and soil. The loss of water through evaporation was determined in the following manner. The checks, containing only soil and water but no plants, were weighed and their loss of moisture through evaporation was determined. The loss was computed as number of grams per square centimeter of surface area. The factor thus obtained from these calculations was used for computing the loss of moisture that resulted in the other jars of the same series. This method of determining moisture losses was found very satisfactory, as will be shown by the results obtained.

Three different soil samples, representing three distinct types; namely, Helemano, Robinson and Waianae, were employed for these studies. The hygroscopic moisture of the three soils ran as follows: Helemano, 2.7 per cent; Robinson, 6.8 per cent; Waianae, 4.4 per cent.

A number of series of cultures, each one containing a certain quantity of soil moisture, were prepared with each soil sample. They contained 5, 10, 15, 20, 25, and 30 per cent of added water in excess of the hygroscopic moisture of the soil. This means that the different soils varied in their total moisture content, but contained the same quantities of added moisture.

The culture jars and their contents were weighed twice each week. The usual method of keeping up the moisture contents at the original percentages was based on the rate of evaporation per square centimeter for each soil at each moisture level as determined by weighings of the check jars. Using the appropriate unit rate of evaporation, water was added in accordance with the surface area of soil in each jar. On a few occasions this was modified on the basis of the actual weights of the several jars and plants. Because of a leak in the glass roof some of the plants got an extra dose of water on one or two occasions, but without prejudice to the general progress of the experiment. At the end of the experiment the moisture contents of the soils were determined and showed but little variation from the required amounts, indicating that the original percentages had been successfully maintained.

EFFECT OF DIFFERENT CONCENTRATIONS OF MOISTURE ON GROWTH OF PINEAPPLES

The growth of pineapple plants at different moisture concentrations is very striking. The plants behaved more or less alike in response to the moisture concentration in all three soils involved in these experiments. The story is better told by the photographs of representative plants shown in plate 1.

Although the fertility and other physical properties of the soils influenced the development of the plants to a certain extent, such influences are negligible in comparison with that of the moisture. Figure 1 shows the effect of both factors discussed, namely, that of moisture and fertility. It indicates that an unusually fertile soil, like Robinson, will grow better plants at the same moisture content than the less favored soils of Helemano or Waianae.

TABLE 1
Moisture evaporation from Helemano, Robinson and Waianae soil series

SOIL TYPE	SERIES AND H_2O CONTENT	TOTAL OF EIGHT PLANT WEIGHTS		DIFFERENCE		WEIGHT OF CHECK PLANTS		
		Initial	Final	Grams	Per cent	Initial	Final	Loss per cent
Helemano	per cent	gm.	gm.			gm.	gm.	
	A: 5	2,572	2,783	⊕ 211	8.2	880	344	64.0
	B: 10	2,682	4,104	⊕1,422	53.0	653	224	65.0
	C: 15	3,011	5,900	⊕2,889	96.0	664	275	58.6
	D: 20	3,046	6,639	⊕3,593	118.0	689	285	60.0
	E: 25	2,692	6,800	⊕4,108	152.6	644	238	63.0
	F: 30	3,631	9,261	⊕5,639	155.3	613	249	60.0
Average	101.2	61.8
Robinson	A: 5	3,624	3,423	⊖ 201	-5.5	804	306	62.0
	B: 10	2,603	3,639	⊕1,047	40.0	623	260	58.3
	C: 15	2,662	5,860	⊕3,198	120.1	602	245	59.3
	D: 20	2,502	6,699	⊕4,207	168.1	595	249	58.2
	E: 25	2,538	6,818	⊕4,280	168.6	619	278	55.0
	F: 30	2,730	7,815	⊕5,085	186.3	558	233	58.2
Average	105.6	58.5
Waianae	A: 5	2,579	2,364	⊖ 215	-8.3	589	249	57.7
	B: 10	3,209	4,422	⊕1,203	37.5	563	257	54.3
	C: 15	2,850	4,883	⊕2,033	71.3	666	307	53.9
	D: 20	3,060	5,533	⊕2,473	80.8	564	203	64.0
	E: 25	3,121	5,671	⊕2,550	81.7	495	231	53.3
	F: 30	2,807	5,785	⊕2,978	106.0	545	203	62.8
Average	62.6	57.7

The growth made by individual plants grown at the same moisture content was not uniform. It must be remembered, however, that the propagation of these plants is not from sexually produced seeds but from asexually produced tissues obtained from different plants of varying potential vitality. If the results obtained in the different cases are considered by groups and not by individuals then the growth curve takes the shape of that appearing in figure 1. It is shown in table 1 that the amount of water lost from the check plants, that is, those that were not planted but left lying on the surface of the soil, was about 60 per cent for the entire period of the experiment. This is of great

TABLE 2

The water distribution of the different series and checks, surface area of each group, and water evaporation per unit of surface area

	CROCK NUMBERS	CROCK SURFACE AREA sq. cm.	TOTAL WATER ADDED gm.	WATER LEFT OVER gm.	WATER USED gm.	TOTAL WATER ADDED gm.	WATER LEFT OVER gm.	WATER USED sq. cm.
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Helemano soil

A {	1+10	1,022	21,462	3,195	18,267	20.99	3.12	17.87
	2—9	4,016	72,627	12,509	60,118	18.09	3.11	14.98
B {	11+20	1,050	28,414	4,021	24,393	27.05	4.82	23.23
	12—19	3,984	95,115	16,655	78,460	23.88	4.18	19.70
C {	21+30	970	31,086	4,935	26,151	32.05	6.09	26.96
	22—29	4,132	125,438	17,802	107,636	30.37	4.32	26.05
D {	31+40	970	34,366	5,790	28,576	35.43	5.97	29.46
	32—39	4,020	140,692	18,535	122,157	35.00	4.60	30.40
E {	41—50	1,014	41,623	6,196	35,427	41.04	6.10	34.94
	42—49	3,984	163,193	21,064	142,129	40.97	5.29	35.68
F {	51—60	1,030	52,024	7,170	44,854	50.51	6.97	43.54
	52—59	4,258	213,360	22,059	191,301	50.12	5.19	44.93

Robinson soil

A {	61+70	1,050	28,896	3,232	25,664	27.47	2.92	24.55
	62—69	4,268	108,650	12,581	96,069	25.43	2.92	22.51
B {	71+80	1,058	29,886	3,639	26,247	28.25	3.44	24.81
	72—79	4,325	120,101	14,826	105,275	27.77	3.42	24.35
C {	81+90	1,074	37,454	5,207	32,247	34.87	4.84	30.03
	82—89	4,276	149,255	17,286	131,969	34.92	4.09	30.83
D {	91+100	1,058	44,263	61.44	38,119	41.83	5.80	36.03
	92—99	4,253	176,456	16,718	159,738	41.50	3.94	37.56
E {	101+110	1,058	44,790	6,719	38,071	42.33	6.35	35.98
	102—109	4,208	189,054	19,046	170,008	44.94	4.54	40.40
F {	111+120	1,034	63,237	6,921	56,316	61.16	6.70	54.46
	112—119	4,268	250,249	26,758	223,491	58.64	6.27	52.37

TABLE 2—Continued

	CROCK NUMBERS	CROCK SURFACE AREA <i>sq. cm.</i>	TOTAL WATER ADDED <i>gm.</i>	WATER LEFT OVER <i>gm.</i>	WATER USED <i>gm.</i>	TOTAL WATER ADDED <i>gm.</i>	WATER LEFT OVER <i>gm.</i>	WATER USED <i>sq. cm.</i>
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Waianae soil

A {	121-130	1,054	26,926	3,000	23,926	25.55	2.85	22.70
	122-129	4,256	101,070	11,182	89,888	23.76	2.64	21.12
B {	131-140	1,070	33,627	4,338	29,289	31.82	4.10	27.72
	132-139	4,216	124,874	16,645	108,229	29.63	3.97	25.66
C {	141-150	1,054	40,657	5,544	35,113	38.57	5.26	33.31
	142-149	4,292	154,424	20,379	134,045	35.98	4.76	31.22
D {	151+160	1,050	54,150	5,938	48,212	51.57	5.66	45.91
	152-159	4,294	204,903	22,889	182,014	47.74	5.35	42.39
E {	161-170	1,038	57,396	6,110	51,286	55.29	5.88	49.41
	162-169	4,020	218,802	27,746	191,056	54.43	6.89	47.54
F {	171-180	1,002	62,351	6,933	55,418	62.23	6.92	55.31
	172-179	3,948	227,427	24,031	203,396	57.60	6.08	51.52

importance, because it shows the great water retention or hydrophilism of pineapple stem tissues. This is probably the main reason why pineapple plants are able to withstand extreme conditions of drought. As it will be noted in table 2, the amount of water that was added to the different jars per square centimeter of exposed surface area was not the same throughout. Certain jars, especially the checks of series A, B, and C of all three soils, with only one or two exceptions, received more water than the others that had plants. This indicates that the water in the check jars evaporated more rapidly than in those containing plants. The decreased evaporation in the jars that had plants resulted from the shading of them. It seems that there is more water lost through evaporation from the soil in the series containing 5, 10, and 15 per cent of water than through transpiration. As the water content of the soil increases however, transpiration also increases. The transpiration water increased over that of evaporation in series D, E, and F in both Helemano and Robinson soils but not in the Waianae soil. We have no other experimental evidence that will explain this condition except the poor growth of the plants and the highly colloidal nature of the soil. It may have happened that the plants grown in the Waianae soil did not transpire as much as the other plants, because of the poor growth they made. It is also possible that water losses through evaporation from a nonshaded clay soil may be more rapid, because of capillarity, than from a shaded soil. The physical texture of the other two soils differed considerably from that of Waianae; the Helemano soil being of a coarse,

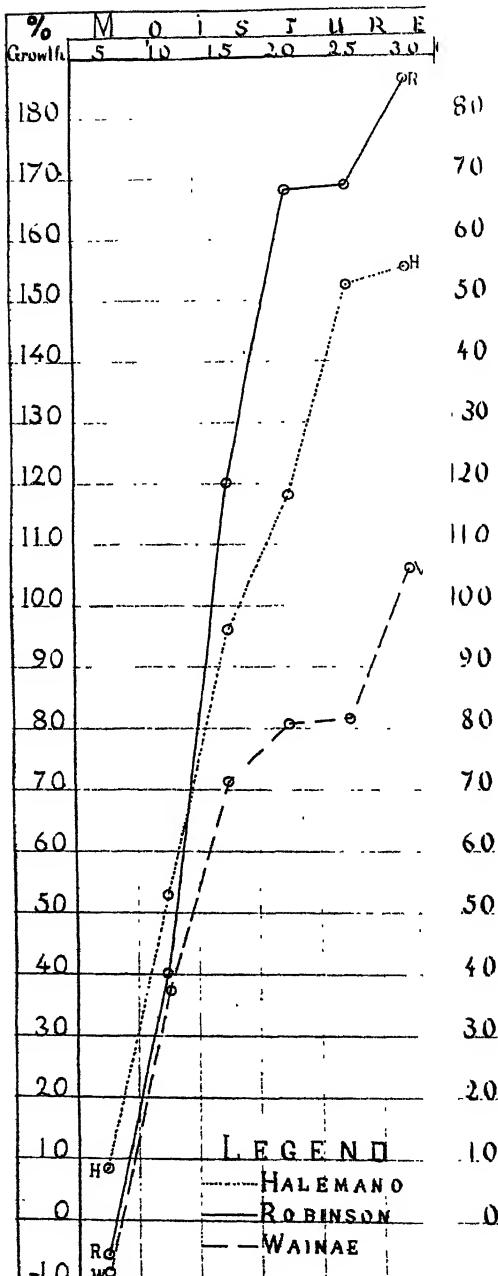


FIG. 1. GROWTH IN PER CENT OF THE INITIAL WEIGHT OF PINEAPPLE PLANTS IN THREE DIFFERENT SOILS; NAMELY, HELEMANO, ROBINSON AND WAINAE, AT 5, 10, 15, 20, 25, AND 30 PER CENT MOISTURE IN EXCESS OF THEIR HYDROSCOPIC MOISTURE

shotty type, and the Robinson a loam, containing a fair amount of humus. It will be noted that some of the checks have received more water than those jars containing plants. This was done with the purpose of maintaining the water content at the same value throughout the series.

A number of interesting features can be observed from these experiments. A comparison of plate 1 with figure 1 shows that there is a very close agreement between the curves of figure 1, on the one hand, and the growth of the root system of the plants as it appears in plate 1. For instance the difference in the growth of the two plants grown in 25 and 30 per cent moisture in plate 1, figure 1 is very small and so is that of the corresponding values in figure 1. In regard to plate 1, figure 2, plants 20 per cent and 25 per cent show but slight difference in growth as do their corresponding values in figure 1. With respect to plate 1 figure 3, we find that plants 15 per cent, 20 per cent, and 25 per cent differ but slightly as do their corresponding values in figure 1.

DISCUSSION OF RESULTS

The relationship of soil moisture to plant growth has been studied quite extensively by various investigators because of its great physiological significance and economic importance. Water plays a most prominent rôle in all stages of the development of living matter. Besides its great importance in the tissues of the plant it serves an equally important function outside of the tissues by dissolving and distributing the different inorganic plant nutrients of the soil. One would, therefore, expect that a decrease in the water content of a soil would have a direct bearing on the concentration of nutrient elements and other such substances of the soil. Because of the development of either higher or lower osmotic forces which may influence the intake of either water or salts, such changes in the soil are capable of modifying considerably the behavior of a plant.

Hume, Loomis, and Hutton (4) in their studies on water as a limiting factor in the growth of sweet clover, found that the minimum water requirements are influenced by the type of soil. For a sandy loam and a silt loam the minimum water content was less than for a clay. Both the sandy loam and the silt loam produced the best growth of plants, whereas the clay produced the poorest. Shive's (8) studies on the relation of soil moisture to physiological salt balance for plants indicate that under unfavorable moisture conditions plants are unable to utilize the salts of the soil and those that are added thereto as fertilizers. Brilliant (1) has found that leaves of *Hedera helix* and *Impatiens parviflora* lose completely their photosynthetic properties when the water content of their tissues decreases between 41 and 63 per cent. Pfeiffer (7) observed the growth of lupines, asparagus, barley, and oats which were grown under two sets of soil moisture conditions; namely, in the one case the soil was maintained at 60 per cent of its water-holding capacity, and in the other the plants were regularly allowed to go without being watered until the moisture content of the soil had fallen to about 30 per cent of its water-holding capacity.

and then the former condition was reestablished. He found that under the alternating periods of drought, the plants did not grow well at all, in comparison with those that had received a constant, full supply of moisture. Clark (2) found that shrubs and trees such as a *Hamamelis virginiana*, *Fagus americana*, and *Quercus alba* contain more water in the spring than in the summer, with an increase again in the fall. Transpiration from the same plants was highest in the spring and lowest in the fall. Maximox and Frei (5) found that plants grown under two sets of conditions, that is, in a soil containing 40 and 60 per cent of its water-holding capacity, produced in the latter case five to six times as great a leaf area as in the former. Shreve (9) has found that the transpiring power of *Encelia farinosa* is inversely proportional to the capacity of the leaf to imbibe water, and directly proportional to the initial water content. Molisch (6) has shown in the case of *Tropaeolum* that the leaves are unable to hydrolyze the starch that they have recently synthesized into sugars under very humid conditions, but that as soon as this condition is modified hydrolysis takes place immediately. The same author believes that the hydrolysis of starch takes place under conditions that are favorable for rapid transpiration. Gray and Pierce (3), in their studies on the rôle of the stomata in the transpiration of certain grains, found that the opening and closing of the stomata depend chiefly upon the light, since they were found to open in light and to close in darkness almost undependently of other factors. If the amount of water in the soil falls below the minimum needed to maintain the turgidity of the guard cells, however, they will remain closed regardless of illumination.

It becomes evident from the above references that soil moisture influences in a number of ways the growth of plants. Low moisture concentrations, by increasing the salt concentration of the soil solution, may render the intake of water by plants more difficult because of the development of higher osmotic forces (10). Aside from the development of such forces, the water supply may not be equal to that required for synthesis and transpiration by plants and for evaporation from the soil. Too high moisture concentrations interfere with normal transpiration processes and, according to Molisch, may interfere with the conversion into sugars of synthesized starches in the leaves and with the translocation of these substances, and thus bring about a halt in the photosynthetic processes of the plant. Too much or too little moisture interferes with the photosynthetic mechanism of plants and hence with their normal development. Using transpiration as an expression of the metabolic activities of a plant, we find that it varies with different moisture and light conditions. Comparing the results obtained in our experiments with those obtained by other investigators on different plants we may be justified in attributing the poor growth of the plants in the series of 5, 10, and 15 per cent of moisture to an insufficient water supply for the normal physiological activities of the plants, and the better growth obtained in the series of 20, 25, and 30 per cent to an ample supply of water. There are certain indications that the photosynthetic mechanism of pineapple plants ceases to function when the moisture content

of the tissues falls below a certain value, the chloroplasts undergoing certain chemical changes under such conditions. Field plants, the root systems of which have been destroyed with a consequent decrease in the moisture content of the leaves below a certain value, manifest changes in the color of their leaves. It has been found that pineapple plants without roots, if left to dry out in the shade do not undergo chromatic changes of their chlorophyl pigments, indicating that light is probably essential for their development.

SUMMARY

Pineapple plants grown in three different soils and at moisture concentrations of 5, 10, 15, 20, 25, and 30 per cent above the hygroscopic moisture of each soil developed as follows:

1. The plants of the series with 5 per cent moisture in the Robinson and Waianae soils did not grow. Some of the plants in the Helemano soil, however, made a very slight growth.
2. The plants in the series with 10 per cent moisture made some growth, but not sufficiently or uniformly enough to be considered as normal.
3. The plants in the series with 15 per cent moisture made a slightly better growth than those of the preceding series. This amount of moisture represents the minimum for the growth of pineapples.
4. The plants of the series with 20, 25, and 30 per cent of moisture made a very good growth indicating that concentrations ranging between 20 and 30 are ample for the growth of pineapples in the majority of soils.

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PLATE 1

EFFECT OF VARIOUS MOISTURE CONTENTS ON PINEAPPLE PLANTS GROWN IN
DIFFERENT SOILS

FIG. 1. Plants grown in Helemano soil.

FIG. 2. Plants grown in Robinson soil.

FIG. 3. Plants grown in Waianae soil.

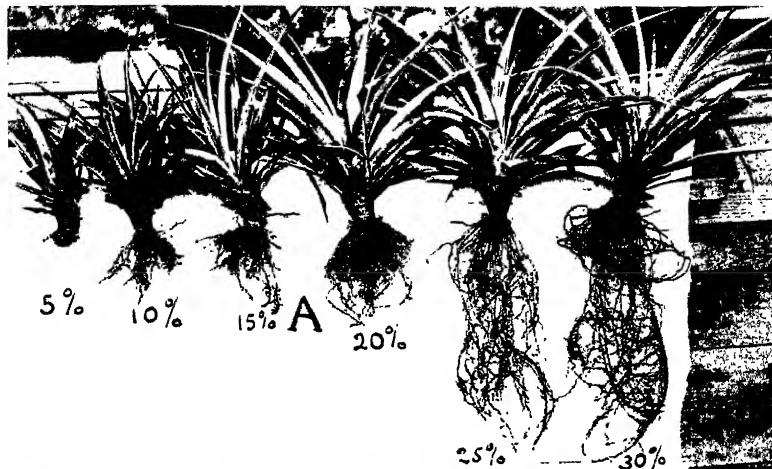


Fig. 1

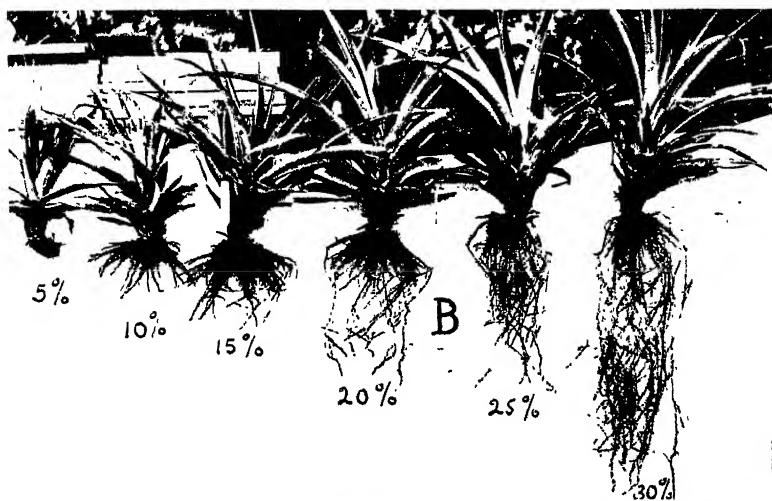


Fig. 2

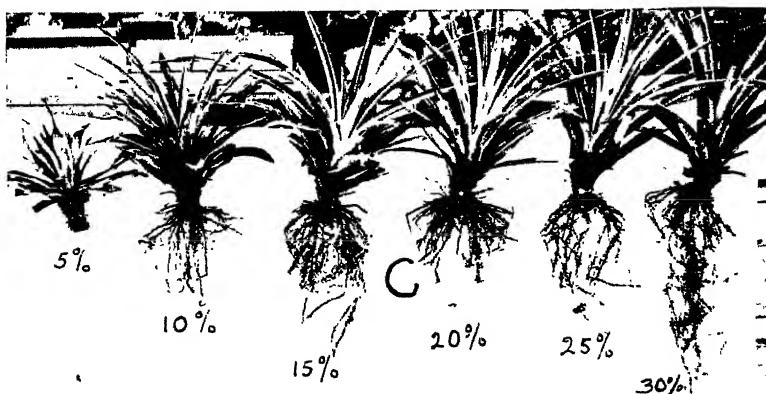


Fig. 3

COLLOIDAL BEHAVIOR OF SOILS AND SOIL FERTILITY: V. THE DISTRIBUTION OF SOLUBLE AND COLLOIDAL IRON AND ALUMINUM IN SOILS

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Aluminum and iron are the two outstanding trivalent cations widely distributed in soils. Their abundance in the earth's crust, 7.81 per cent and 5.46 per cent respectively, (1) makes their presence in the soil imperative.

A survey of the chemical properties of these cations shows that in general very few of their compounds are capable of remaining in solution in a medium close to neutrality, or even slightly to fairly acid. They precipitate readily either as the hydroxides or phosphates, if the latter are present.

In nature very small amounts of the water-soluble compounds of aluminum are found. Most of the aluminum is locked up in the feldspars and other minerals, but primarily aluminum is combined with silica. Iron, which is isomorphous with aluminum is—in its ferric compounds—in general similar to aluminum, or even less soluble.

It is known that the so-called insoluble compounds and mineral complexes of aluminum and iron are gradually being attacked by the forces of weathering; some of the iron and aluminum go into solution only to be again precipitated or washed down into the lower layers, or go even further and move with the ground waters.

The soluble iron and aluminum in the normal soil under the conditions of the prevailing reactions and other secondary factors tend to be transformed into the colloidal state, either sol or gel, or both. The orstein formation or the so-called "hardpan," the lateritic formations, and many others are nothing more than a resultant of the movement of iron and perhaps aluminum (the rôle of aluminum gels in cementing materials in the soil has not as yet been extensively investigated) in the soil and their formation from the molecular into the sol and gel states.

From the standpoint of the genetic school of soil classification iron and aluminum are chemical agents of prime importance in the soil-forming processes, inasmuch as the leaching and deposition reactions connected with these elements influence the type of soils.

It is the colloidal behavior of iron and aluminum that determines their presence or absence in the soil solution and thus influences the relations in the plant-soil systems.

The evaluation of the iron and aluminum problem in soil fertility involves a study of the transformation stages of the iron and aluminum compounds, the conditions responsible for their solubility, and also their elimination from the sphere of action (distribution and movement) as they are converted in soils and gels. The experiments reported are an attempt to throw some light on one of the phases of the problem, namely, the distribution of iron and aluminum in soils.

EXPERIMENTAL

Elsewhere (2) the course of the reactions involved in the transformation stages of Fe and Al were discussed. Solutions, 0.0075M, of Al and Fe in the form of their salts of Cl, NO₃, SO₄, and PO₄ were studied for the state of aggregation of the colloids formed in the presence of these anions.

TABLE 1

Gel formation and persistence of molar state of Al and Fe in the presence of the inorganic anions PO₄, SO₄, Cl, and NO₃

KIND OF ANION	REACTION LIMITS OF COMPLETE COAGULATION OF		REACTION LIMITS AT WHICH THE MOLAR STATE CEASES TO BE PRESENT		REACTION RANGE AT WHICH THE SOL STATE EXISTS	
	Al	Fe	Al	Fe	Al	Fe
PO ₄	3.2	3.2	3.2	3.2	*	2.2-3.4
SO ₄	4.8	3.8	4.5	3.2	4.3-5.6	2.4-5.2
Cl.....	5.8	5.5	5.1	4.6	4.4-5.9	2.4-5.2
NO ₃	6.0	5.4	5.9	4.0	4.0-4.8	2.4-4.4
SO ₄ + Cl + NO ₃ combined	4.9	4.7	4.8	2.8		

* No sol state of Al exists in the presence of the SO₄ anion.

Table 1 is a summary of the effect of the anions on the states of aggregation of Al and Fe.

Assuming that besides the anions there are no other side reactions which might influence the solubility and state of aggregation of the Al and Fe in the soil one may readily see from the data presented in table 1 that under normal soil conditions the chances for soluble Al or Fe are meager. The reaction limit for the existence of the molar state of Al in the presence of the NO₃ anion, pH 5.9, is within the range of soil reactions in the humid regions. Under conditions of intense nitrification there is the possibility of Al being in solution, especially within the sphere of the so-called "local action," in close proximity of the roots and at centers of active nitrification. One must not forget, however, that all soils contain, besides the NO₃ anion, almost always some SO₄ and PO₄ anions. In the presence of these, as shown in table 1, the reaction points of molecular dispersion and gel formation shift toward the point which is characteristic for the SO₄ or PO₄ anions. In other words the

low coagulation capacity of the monovalent NO_3^- anion is masked by the high coagulation capacity of the divalent and trivalent anions. The reaction at which the sol state of Fe and Al exists as given in table 1 shows a considerable range. This means that with the disappearance of the molecular

TABLE 2
Fertilizer treatment of plot soils used in the dialysis experiments

PLOT NUMBER†	FERTILIZER TREATMENT—1908-1923	FERTILIZER TREATMENT—1923-1927
1A, 1B	Nothing	Nothing
2A, 2B	16 pounds muriate of potash	8 pounds muriate of potash
3A, 3B	32 pounds acid phosphate	16 pounds superphosphate
4A, 4B	Minerals only*	Minerals only*
5A, 5B	Minerals and 1600 pounds cow manure	Minerals and 1600 pounds cow manure
6A, 6B	Minerals and 1600 pounds horse manure	Minerals only
7A, 7B	Nothing	Nothing
8A, 8B	Minerals and 8 pounds NaNO_3	Minerals and 8 pounds NaNO_3
9A, 9B	Minerals, and 16 pounds NaNO_3	Minerals and 16 pounds NaNO_3
10A, 10B	Minerals and $\text{Ca}(\text{NO}_3)_2$ equivalent to 16 pounds NaNO_3	Minerals and $\text{Ca}(\text{NO}_3)_2$ equivalent to 16 pounds NaNO_3
11A, 11B	Minerals and $(\text{NH}_4)_2\text{SO}_4$ equivalent to 16 pounds NaNO_3	Minerals and $(\text{NH}_4)_2\text{SO}_4$ equivalent to 16 pounds NaNO_3
12A, 12B	Minerals and CaCN_2 equivalent to 16 pounds NaNO_3	Minerals and CaCN_2 equivalent to 16 pounds NaNO_3
13A, 13B	Minerals and dried blood equivalent to 16 pounds NaNO_3	Minerals only
14A, 14B	Minerals and fish equivalent to 16 pounds NaNO_3	Minerals and $\text{NaNO}_3, (\text{NH}_4)_2\text{SO}_4$ (N half and half)
15A, 15B	Minerals and concentrated tankage equivalent to 16 pounds NaNO_3	Minerals and tankage equivalent to 16 pounds NaNO_3
16A, 16B	Minerals and 200 pounds alfalfa hay	Minerals only
17A, 17B	Minerals and 200 pounds wheat or rye straw	Minerals only
18A, 18B	Minerals and 1600 pounds cow manure and 16 pounds NaNO_3	Minerals and 1600 pounds cow manure and 16 pounds NaNO_3
19A, 19B	Minerals only	Minerals only
20A, 20B	Minerals and 200 pounds wheat or rye straw and 16 pounds NaNO_3	Minerals and 200 pounds rye straw and 16 pounds NaNO_3

*Minerals—32 pounds acid phosphate and 16 pounds muriate of potash *Minerals—16 pounds superphosphate and 8 pounds muriate of potash

† The area of each one of the plots is $\frac{1}{16}$ acre.

state of aggregation the sol state may still persist. The question arises—and this has been discussed in a former paper (2)—whether plants take up substances in the colloid state. In this connection it is to be remembered that the size of the particles increases as the gel state is approached. In terms of

reaction as presented in table 1, it means that with the increase of the pH value the size of the particles of Al and Fe increases and it will be more difficult to reconcile the idea of sols—approaching the gel state—being absorbed by plants. It is at the lower pH values, a condition not encountered in normal soils, that one may expect absorption of sols which in their state of aggregation approach molecular dimensions.

All of this leads us to believe that most of the Al and Fe which in the process of soil formation has split off from the insoluble silicates, either moves down-

TABLE 3
Molecular and sol state of aggregation in 100 gm. of plot soils (surface), 1926

PLOT NUMBER	A PLOTS				B PLOTS			
	Reaction before dialyzing soils	Molecular Al_2O_3 and Fe_2O_3 dialyzed	Al_2O_3 and Fe_2O_3 as sol in leachings	Reaction after dialyzing soils	Reaction before dialyzing soils	Molecular Al_2O_3 and Fe_2O_3 dialyzed	Al_2O_3 and Fe_2O_3 as sol in leachings	Reaction after dialyzing soils
1	pH 5.4	1.0	0.8	pH 5.4	pH 7.2	1.0	0.66	6.5
2	5.2	0.0	0.26	5.2	7.2	0.0	0.66	6.6
3	5.2	0.0	0.0	5.4	7.0	1.5	0.53	6.6
4	5.3	0.0	1.06	5.4	7.1	3.6	1.06	6.8
5	5.7	1.2	0.8	5.5	7.0	0.0	0.0	6.8
6	5.2	1.8	0.53	5.4	7.1	2.3	0.0	7.0
7	5.0	1.4	0.26	5.2	7.0	0.0	0.53	6.8
8	5.6	0.9	0.93	5.8	7.0	0.0	0.0	6.6
9	5.6	0.0	0.53	6.0	7.1	1.0	0.0	7.0
10	5.6	0.6	0.53	6.0	7.1	0.0	0.0	6.8
11	4.2	2.8	0.5	5.0	6.1	0.2	1.1	
12	5.8	0.0	1.5		7.4	0.2	0.0	
13	5.2	0.0	0.6		6.9	0.4	0.6	
14	5.3	0.7	0.0		6.9	0.2	0.2	
15	4.9	1.4	0.6		6.8	1.2	0.2	
16	4.9	0.6	Lost		6.9	0.9	0.0	
17	5.3	0.1	0.0		6.9	0.7	0.0	
18	5.6	0.0	0.5		7.0	0.0	0.0	
19	5.1	0.4	0.0		7.0	0.0	0.3	
20	5.4	0.3	1.3		7.3	0.0	0.0	

ward—partly—or is precipitated at certain points under certain conditions in the soil profile.

To determine the state in which Al and Fe are found in soils the dialysis method has been employed. One hundred grams of soil was placed into 250-cc. collodion bags, 100 cc. of water added and dialyzed in distilled water until no test for Fe or Al was obtained in the dialyzate. To facilitate rapid dialysis the bags were shaken up from time to time. After that the soil from the collodion bags was removed, placed on a paper filter, and leached to a volume of 200 cc. The leachings represent the colloids present in the sol state, as the ordinary filter paper does not retain any of the colloids in that state.

The soils from the soil fertility plots, A and B series, of the New Jersey Station were used for this work. The A plots are unlimed and the B plots are limed every 5 years. Table 2 gives the plan and treatment of the soils from the plots.

These plots, because of their history, are well adapted for studies in colloidal behavior. The various treatments ought to show any difference inherent to the particular treatment. The only objection to a study of the distribution of the state of Fe and Al in these plot soils is the necessity of working with

TABLE 4
Molecular and sol state of aggregation in 100 gm. of plot soils (subsoil), 1926

PLOT NUMBER	A PLOTS			B PLOTS		
	Reaction before dialyzing soils	Molecular Al_2O_3 and Fe_2O_3 dialyzed	Al_2O_3 and Fe_2O_3 as sol in leachings	Reaction before dialyzing soils	Molecular Al_2O_3 and Fe_2O_3 dialyzed	Al_2O_3 and Fe_2O_3 as sol in leachings
1	5.54	1.0	0.8	6.67	0.3	0.8
2	5.56	Lost	1.0	6.84	0.4	0.5
3	5.24	0.9	2.2	6.77	0.5	1.5
4	5.49	0.0	0.0	6.93	0.4	0.7
5	5.31	0.2	0.0	6.92	0.8	0.7
6	5.05	0.7	1.0	6.88	1.0	0.7
7	5.34	0.0	0.0	6.60	0.0	0.5
8	5.73	0.0	0.0	6.91	0.8	0.7
9	5.8	0.5	1.6	6.99	0.8	0.9
10	5.5	0.0	5.0	6.85	Lost	1.2
11	4.83	1.1	0.0	5.97	0.6	1.4
12	5.43	0.2	0.0	6.79	0.4	0.5
13	5.54	1.2	0.0	6.77	0.8	1.0
14	5.0	0.4	0.4	6.75	0.8	0.6
15	5.42	0.6	0.0	6.67	0.6	1.0
16	5.12	0.5	2.0	6.77	1.1	0.8
17	5.39	0.0	3.2	6.67	1.0	1.0
18	5.6	0.6	1.7	6.67	Lost	1.0
19	5.19	1.1	0.2	6.83	0.3	0.7
20	5.44	0.0	6.4	7.14	0.6	1.0

samples obtained by borings. As the experiments on these plots are still in progress the soil could not be disturbed to the extent of making profile cuts for a complete survey of the distribution of the various colloidal materials.

Accordingly, 100-gram samples from the A and B plots were placed in collodion bags and dialyzed as described, then filtered and Fe and Al determined on the dialyzates and leachings, respectively.

Table 3 gives the results on the A and B plots, surface soil; table 4 gives the results on the A and B plots, subsoil. Let it be noted at this point that the precipitates as recorded in tables 3 and 4 are primarily Al and Fe. There

are, however, admixtures of silica, especially in the data on the sol state. But the amount is so small that it cannot be determined unless larger quantities of soil are used for dialysis and leaching. The bulk of the precipitates consists of Al and Fe. One may readily see that very little of the molecular or sol state of Al and Fe exists in the soil as exemplified by the plot samples which vary in reaction and fertilizer treatment. The largest amount of Al and Fe may be found in the surface soil of plot 11A (see table 3). Table 2 tells us that this plot has been treated with $(\text{NH}_4)_2\text{SO}_4$ for the last 20 years. The soil is very acid—pH 4.2. It is characteristic that the reaction of this soil and the amounts of Al and Fe found correspond very well with the findings of the pure chemical studies as reported elsewhere (2), namely, that the SO_4^- anion prevents the formation of the sol state. Only 0.5 mgm. of Al and Fe was found in the leachings after dialysis. It is to be remembered that after dialysis, with the removal of the electrolytes, the degree of the dispersion of the colloid substances increases. Still but traces of Al and Fe could be found in the leachings as the sol. Apparently the negatively charged divalent SO_4^- anion has been absorbed by the colloids, and in this manner, or by virtue of electrical discharge, the gel state of the Al and Fe exists. In the plot 11B (limed) practically no molecular state of Al and Fe was found, showing that the reaction and anion effects are at work in controlling the state of aggregation of these colloids.

Although there is no consistent correlation between the treatment of the soils and the state of aggregation of the colloids in them, one may detect the tendency of organic manures to give slightly more dialyzable Al and Fe; and examination of the data in table 3 shows that in general minerals tend to coagulate the colloids, which is in accordance with the fundamental laws of colloid chemistry that electrolytes tend to coagulate colloids.

The amount of Al and Fe in molecular state in the surface soil (table 3) is greater than in the sol state. The reverse is true in the subsoil (table 4). This may be explained on the basis of electrolytes present in the respective soil layers. The subsoils had more electrolytes thus tending to decrease the degree of dispersion of the colloids.¹

In the subsoils of plot A the sesquioxides dialyzed consisted primarily of Al; in the leachings there was a considerable amount of Fe. This shows that the Fe precipitates first while the Al may still remain in the molecular state.

In general, however, it may be said that the quantities of Fe and Al existing in the soil in the molecular state are very small. Even plot 11A with a reaction of pH 4.2 has only 28 p.p.m.

At this point it may be of interest to record a number of dialyses and extraction experiments conducted with large amounts of soil from plot 11A, which has been receiving ammonium sulfate treatments for 20 years. Five

¹ This has been proved by conductivity measurements and by weighing the residue left in the dialyzates. An examination of the climatological data reveals the facts that the samples have been taken after a rain, a factor which would bring about such a condition.

portions of 300 grams of soil were placed in collodion bags and dialyzed until no test for iron or aluminum could be detected in the dialyzate, and the total amount of Al_2O_3 and Fe_2O_3 was determined. It was found that 26.6 p.p.m. of Al_2O_3 and Fe_2O_3 dialyzed. Another set of 300 gram portions of soil from plot 11A were extracted with water, filtered, slightly acidified, and the total Al_2O_3 and Fe_2O_3 determined. Again the amount was 26.6 p.p.m. This shows that there was no sol state of Al and Fe in this soil and it corroborates the findings reported elsewhere (2) that in the presence of the SO_4^{2-} anion, no Al exists in the sol state. In this case, even the Fe did not appear in the sol state.

In order to prove the existence of the gel state of the respective colloids, Fe and Al, 10-gm. samples of soils from the A plots were extracted with 250 cc. of *N* BaCl_2 solution. The extract was acidified and ammonia added so that there would be an excess of NH_4Cl to prevent the precipitation of the $\text{Mg}(\text{OH})_2$.

TABLE 5

*Titrable acidity, Al_2O_3 , and Fe_2O_3 in 250 cc. *N* BaCl_2 on 10 gm. of soil extract from the A plots*

PLOT NUMBER	TITRABLE ACIDITY: 0.02 <i>N</i> KOH	Al_2O_3 AND Fe_2O_3	Fe_2O_3	PLOT NUMBER	TITRABLE ACIDITY: 0.02 <i>N</i> KOH	Al_2O_3 AND Fe_2O_3	Fe_2O_3
	cc.	mgm.	per cent		cc.	mgm.	per cent
1A	5.1	1.4		11A	12.2	3.7	34.0
2A	6.6	3.6	35.0	12A	1.3	2.1	41.9
3A	6.4	3.2		13A	6.2	1.0	33.3
4A	5.5	1.6		14A	5.1	1.8	18.3
5A	4.9	1.2		15A	4.7	1.6	
6A	5.3	2.3		16A	5.8	2.6	33.9
7A	5.7	1.6		17A	4.9	2.6	
8A	3.8	1.4	19.0	18A	2.8	1.6	
9A	3.6	1.2		19A	6.1	1.2	
10A	3.7	2.6		20A	3.0	1.2	

The precipitate was filtered, redissolved with nitric acid, and reprecipitated from hot solution with 1:1 NH_4OH .

Table 5 gives the titrable acidity, the amounts of Al_2O_3 and Fe_2O_3 (traces of P could be demonstrated, but the quantities were so small that determinations were not made) in the extracts as well as a few determinations of the percentage of Fe_2O_3 in the combined precipitate.

The significant feature of the data in table 5 is the large increase in soluble iron and aluminum as compared with the amounts found by dialysis and water extraction.

An analysis of the reactions responsible for the appearance of the soluble iron and aluminum upon extraction with the *N* BaCl_2 solution may not be out of place. The soils from the A plots are partially unsaturated, e.g., the complex capable of base exchange contains, besides other cations, some H ions. These were replaced by the Ba ions thus forming HCl , which in turn

reacted with the gels of iron and aluminum bringing the Fe and Al into true solution.

When a second extraction with BaCl_2 solution was made on the same soils followed by leaching with more BaCl_2 solution, more Fe and Al could be found. None was found when the H-ion concentration of the leachings reached a point at which no aluminum in the molecular state could exist in the presence of the Cl anion, namely at pH 5.4 to 5.6. The amount of Fe and Al extracted with the BaCl_2 solution does not therefore represent the total of Fe and Al present in the gel state. It proves, however, the point that the Fe and Al exist in the gel state. In order to get all of the Fe and Al present in the gel state the soil could be treated with 0.05 N HCl. This phase of the problem, is now being looked into.

The figures on the percentage of Fe show that less of the Fe gel than of the Al gel goes into solution with the acid produced by the replacement process. This is in accordance with the pure salt studies reported (2), whereby the Fe requires a greater concentration of acid in order to go into solution.

A word is to be said about the figures on titratable acidity as reported in table 5. In general a larger amount of acid corresponds to a higher Fe and Al content; there are, however, exceptions. It is very likely that the age of the gel has something to do with the speed of its solubility. This is especially true for the Fe, a phenomenon clearly manifesting itself in the process of laterization. Undoubtedly some of the Al gel, upon aging, is converted into an insoluble form, perhaps gibbsite.

SUMMARY

1. From a study of the anion effect and reaction of disperse medium on the condition of state of iron and aluminum in soils it is clear that as far as the inorganic compounds of iron and aluminum are concerned the molecular state of either one of these two cations rarely persist in the soil. It is very likely that within the sphere of "local action," in close proximity of the roots or around centers of active nitrification, soluble iron and aluminum do exist temporarily. This may be one of the sources of iron for plants, as has been pointed out (2).

2. Colloidal iron and aluminum sols of various degrees of dispersion may exist, especially in the presence of the NO_3^- anion and at moments of the relative absence of the SO_4^{2-} and PO_4^{3-} anions.

3. Dialysis experiments on samples of surface and subsoil from the soil fertility plots of the New Jersey Experiment Station prove that only extreme conditions of acidity, like those on plot 11A which barely supports plant life, may bring about iron and aluminum in the molecular state.

4. Water extracts of the dialyzed soils should contain the iron and aluminum which may be present in the sol state, and in experiments with a large number of soils it was found that very little of the sol state exists.

5. Fertilizer treatments of the soils investigated do not seem to show marked effects on the state of aggregation of the iron and aluminum. The mineral fertilizers tend to coagulate the colloids.

6. The bulk of the iron and aluminum split off from the mineral complexes in the process of weathering exist in the soil as the gel, and, as such, are distributed throughout the soil profile.

7. BaCl_2 extracts of the same soils which were used in the dialysis experiments give large amounts (as high as 370 p.p.m.) of iron and aluminum. This is due to the solubility effects of the acid produced by the release of H ions in the process of replacement with the Ba ion. The HCl thus formed reacts with the gels, bringing them in solution.

8. The relation of the acid formed by the base exchange reactions to the amounts of iron and aluminum going in solution is discussed. It is shown that the iron and aluminum going in solution do not represent the total quantity of gel present in the soil.

9. A certain correlation may be found between the amount of titratable acidity of the acid produced by replacement and the amount of iron and aluminum in solution.

10. Less iron than aluminum goes into solution as a result of the acid produced by the replacement process. It is suggested that the aging of the colloids have something to do with this phenomenon.

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- (1) CLARK, F. W. Data on geochemistry. *U. S. Geol. Survey Prof. Paper* 14: 108
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BOOK REVIEW

Physiology and Biochemistry of Bacteria. Vol. 1. Growth Phases; Composition and Biophysical Chemistry of Bacteria and their Environment; and Energetics. By R. E. BUCHANAN, Dean of the Graduate School, professor of Bacteriology, and Bacteriologist of the Iowa Agricultural Experiment Station, Iowa State College, and E. I. FULMER, Professor of Biophysical Chemistry, Department of Chemistry, Iowa State College. Williams and Wilkins Co., Baltimore, Md., 1928. Pp. xi and 516, fig. 78. Price \$7.50.

- One has reason to become enthusiastic over the prospects of a reference book (or books) upon the physiology of microorganisms. The material is widely scattered in journals devoted to general biology, medicine, industrial sciences, and various branches of chemistry. Furthermore, the subject has never received comprehensive treatment in the English language and the only available extensive treatise is that by Kruse (*Allgemeine Mikrobiologie*, 1910) which, although still very helpful, needs revision and extension to include recent advances in the subject.

It is difficult to estimate properly the value of this volume by itself, because it is presumably but one of two volumes on the subject. This first volume is divided into five chapters: (1) Introduction—3 pages, (2) Growth phases and growth rates in cultures of microorganisms—59 pages, (3) Chemical composition of the cells of microorganisms—76 pages, (4) Physico-chemical and physical characteristics of microorganisms and their environment—234 pages (5) Energy relationships, growth and movement of microorganisms; Energetics—88 pages, Bibliography—31 pages.

"In most cases historical discussion has been reduced to a minimum." That the subjects are not considered in a comprehensive bibliographical manner may be apparent from the fact that about 670 references are cited, many of which are concerned only indirectly with the physiology of microorganisms. One may be justified in considering this volume as an introduction to the more complicated phenomena of microbial physiology yet to be considered. Although much of the information on microbial physiology is treated briefly, or not at all, this may be expected in view of the fact that volume 2 (yet to appear) is devoted to the influence of environmental conditions on microbial development, changes produced by bacteria, and the mechanism of such changes.

To the reviewer, the subject matter lacks continuity as a result of apparently too great emphasis upon basic physical and physico-chemical data. Of the 461 pages of the book, much less than half is concerned with subjects logically considered as microbial physiology. The majority of the text is devoted to ex-

tensive treatment of the basic physico-chemical principles such as estimation of concentrations of solutions, surface tension, absorption, osmotic pressure, diffusion, specific heat, boiling points, light emission, reflection, absorption and transmission, electrical measurements of conductivity, H^+ and OH^- concentrations and oxidation and reduction potentials, colloids, types of work and energy, and means of their estimation. Over 50 pages are concerned with the subject of measurement and explanation of hydrogen and hydroxyl ions alone, with little or no suggestion of the response of microbial cells to different concentrations of these ions. It is far from the intension of the reviewer to underestimate the importance of this subject material to all biologists, but it is seriously questioned whether the bacteriology text is the logical place for the dissemination of fundamental physics and physical chemistry. The authors express their attitude as follows:

" It is evident that physical bacteriology includes all the applications of mathematics, physiology, chemistry, and physics to the problems of life and growth of microorganisms." To this statement the reviewer does not take exception, unless the bacteriologist assumes that it implies that he must be the teacher of *fundamental* mathematics, physiology, chemistry, and physics.

As a reference text upon principles of physics and physical chemistry of interest to biologists the book may become of much more value than as a source book or text on the physiology of microorganisms. The subject matter as a whole is presented in very clear style and has a comparatively limited number of errors in text.

R. L. STARKEY.

ADSORPTION OF POTASSIUM FROM DIFFERENT SOURCES AND NITRIFICATION STUDIES WITH NORFOLK SANDY LOAM¹

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The work presented in this paper was done in connection with a series of fertilizer experiments with potatoes conducted at Snow Hill, Maryland, and reported elsewhere (12). Briefly, these experiments were planned in order to study the effects of potassium from three different sources and applied at different rates, on the yield of early potatoes and sweet potatoes. Potassium chloride, potassium sulfate, and manure salts (20 per cent) were used as the sources of potassium. The soil on which the experiments were located is a Norfolk sandy loam, very deficient in nitrogen, phosphorus, and potassium, and subjected to considerable leaching during wet seasons. Because of these conditions, and also because of the importance of nitrogen and potassium in potato production on this soil the following work was conducted. The present investigations were carried out in order to study the relative adsorption of potassium from the different materials used, and to determine the effects of these materials on the nitrification of dried ground fish, packing house tankage, and sulfate of ammonia.

ADSORPTION OF POTASSIUM FROM DIFFERENT SOURCES

For almost a century, investigators have known that soils in general possess the power to decrease the concentration of salt solutions with which they are brought in contact. As early as the latter part of the Eighteenth Century much work had been done on the subject and considerable data had been accumulated. This earlier work has been compiled and reviewed in detail by Patten and Wagaman (18). Of the early investigations, the classical work of Way, Frank, Treutler, and Peters, is perhaps the most outstanding. Way (27), as early as 1850 found an excess of bases held by sand treated with salts. Frank (6), in one of his percolation experiments, found 95.5 per cent of the potassium of a 0.1 per cent solution of potassium chloride retained by an 18-inch column of soil. Treutler (25), found that additions of sodium chloride reduced the amount of potassium retained by soils treated with solutions of

¹ Part III of a thesis submitted to the graduate faculty of the University of Maryland, June, 1928, in partial fulfillment of the requirements for the degree of doctor of philosophy.

² The author takes this opportunity to thank Dr. L. W. Erdman for his many helpful suggestions in carrying out this work and for reading the manuscript.

potassium chloride thus confirming the earlier work of Frank (6). However, Fisher (5), in a more recent publication, presented the work of Lemberg which shows a replacement of sodium by potassium in soils. It was pointed out that under similar conditions, potassium will replace sodium, as might be suggested by the retention of large amounts of potassium by soil, in comparison to sodium. Furthermore, the presence of sodium chloride rather than potassium chloride in the ocean is suggestive of the relative amounts of these two salts that may be held by soils.

Patten and Waggaman (18) recalculated the results obtained by Peters (20) on the removal of potassium chloride from solution by soil. The recalculated results show that the removal of potassium from a weak solution was nearly twice as great as from a solution twenty times stronger.

Schreiner and Failyer (21) percolated a potassium chloride solution containing 200 p.p.m. of potassium through a short column of sandy loam soil at the rate of 50 cc. in 24 hours. The first 200 cc. of percolate was reduced to 96 p.p.m. of potassium and thereafter the amount of potassium in the percolate steadily increased. It was concluded that the potassium retained by soil is continually diffusing into the free soil solution and becoming directly accessible to plants.

McCall, Hilderbrandt, and Johnston (16) studied the adsorption of potassium by a sandy loam soil from a solution of potassium chloride containing 62 p.p.m. of potassium. After the first 10 minutes in contact with the soil, the solution was reduced to 40 p.p.m. of potassium, and to 36 p.p.m. after the second 10-minute period. From this point the adsorption gradually decreased until the solution coming from the soil was almost unchanged. The removal of the absorbed potassium by distilled water was greatest at first, and then became practically constant. About 42 per cent of the absorbed potassium was still retained by the soil after six leachings had been made.

Frear and Erb (7) stated that much of the potash applied as fertilizer remained in the surface soil in a state highly available to crops, and that the loss by drainage was probably not great. McGeorge (17), using a sandy textured soil from Honolulu, obtained as high as 45 per cent potassium fixation by leaching with a solution of potassium sulfate containing 214 p.p.m. of potassium.

Starkey and Gordon (23) showed that the hydrogen-ion concentration affected adsorption. Potassium was adsorbed in largest amounts by hydrogel of silica in an alkaline solution but when the reaction was made acid, the amount of potassium adsorbed was markedly reduced.

Summarizing the work of previous investigators, it is evident that potassium is adsorbed by soils in varying amounts depending upon the existing conditions, kind of soil, and the amount and kind of potassium material applied. From a practical standpoint this adsorption is of considerable importance. In the case of potato growers in Maryland and Virginia, where at the present time annual applications of from 1000 to 2000 pounds of fertilizer per acre,

analyzing from 5 to 8 per cent potash, are made, the subject demands unusual attention. Moreover, in the potato-growing sections of these two states, the practice of using larger amounts of potassium in the fertilizer mixtures is probably increasing rather than decreasing. Finally, the loose, friable condition of Norfolk sandy loam, which is used extensively for growing early potatoes and sweet potatoes, adds further interest to the problem. In consideration of these facts the following work was undertaken.

PRELIMINARY EXPERIMENT

A series of 10 leaching cylinders similar to those described by Smith (22) were set up and each was filled with 5500 gm. of Norfolk sandy loam soil. This soil was obtained from the surface soil of the experimental fields at Snow Hill, Maryland, and was mixed thoroughly and screened to remove remains of

TABLE 1
Mechanical analysis of Norfolk sandy loam soil used in preliminary experiment

	per cent
Fine gravel.....	1.2
Coarse sand.....	12.0
Medium sand.....	12.6
Fine sand.....	46.4
Very fine sand.....	8.2
Silt.....	15.3
Clay.....	4.4
Water-holding capacity.....	29.2
Total nitrogen.....	0.0766
Total potassium.....	0.8847
pH.....	6.4

plants and other coarse material. The mechanical analysis of this soil as determined by the U. S. Bureau of Chemistry and soils is given in table 1.

Applications of 5.5 gm. of fertilizers analyzing 7-6-5, 7-6-8, and 7-6-10 were mixed with the upper 3 inches of soil in each cylinder. This application corresponds to a broadcast application of 2000 pounds per acre. Potassium sulfate, potassium chloride, and manure salts were used alone to supply equivalent amounts of potash at all three rates, so that three sources of potassium could be compared for each rate of application. The phosphoric acid was supplied by 16 per cent superphosphate and the nitrogen was supplied by nitrate of soda, sulfate of ammonia, packing house tankage, and dried ground fish in equivalent amounts from all four sources. One cylinder was treated with a 7-6-0 mixture for a check. The cylinders were leached every two weeks for 16 weeks with 860 cc. of distilled water, and the leachings were collected for analysis. This rate of leaching approximated the average rainfall during the growing season of the early potato crop at Snow Hill, Maryland, which amounted to 11 inches.

Potassium determinations were made gravimetrically following the method described by Stewart (24), using a 300 cc. aliquot. At the start, it was planned to determine the amount of potassium in each series of leachings in order to calculate the loss of potassium from the soil, but the results of the determinations on the first three series of leachings made a change in the work necessary. Only traces of potassium could be detected in the leachings for the first three series after 2580 cc. of distilled water had been added. Consequently, it was decided to restrict the study to the translocation of potassium in the soil.

The leachings were continued at the regular intervals, and after the last leaching had been made, the soil in each cylinder was sampled by taking a boring of the entire depth of the soil column with a brass tube. The soil column thus obtained was divided into three equal portions. The middle portion was discarded and total potassium determinations were made on the upper and lower portions using the official method (1). The results of these determinations showed no significant differences in the potassium content of the soil at the different depths, regardless of the amount and source of potassium used.

From this preliminary work it would seem that, regardless of the sandy texture of this soil, there was an appreciable adsorption of the potassium applied. An experiment was then planned to determine the relative rate of potassium adsorbed from strong solutions of potassium salts, in order to arrive at the adsorption capacity of the soil.

DESCRIPTION OF APPARATUS

To carry out the leaching work, the simple apparatus shown in plate 1 was set up. Before adding the soil to the extraction funnel, a few pieces of HCl-washed gravel were placed in the bottom so that the soil would not clog the outlet during leaching. The outlet tube in the reservoir was provided to maintain atmospheric pressure above the liquid in order to permit a constant flow of solution from the bottle. By carefully regulating the flow of solution in and out of the extraction funnel, it was found possible to maintain about an inch of "head" over the soil and thus prevent channeling. Difficulty was encountered in regulating the flow at a slow rate, but with care the rate was so reduced as to permit 2 liters of solution to pass through in about 60 hours. The extraction funnel was charged each time with 200 gm. of air-dry Norfolk Sandy loam which had been passed through a 20-mesh sieve. The apparatus was set up in the laboratory where a temperature of about 22°C. obtained throughout the experiments.

Samples of the soil were leached with solutions of different C. P. potassium salts and the potassium content in each leaching was determined gravimetrically (24). The hydrogen ion concentration of each leaching was determined electrometrically using a Hildebrand bubbling electrode. Conductivity measurements were made at 23°C. with a Kohlrausch bridge according to the method described by Findlay (4). Immediately after each leaching was com-

pleted, 1 liter of 0.05 *N* HCl was passed through the soil and the leachings collected in 500-cc. fractions. This procedure was similar to that described by Gedroiz (8) in determining the replaceable bases in soil. The same determinations were made on each fractional leaching as were made on the leachings from the salt solutions. The results from these determinations are shown in table 2.

It will be seen from table 2 that Norfolk sandy loam seems to be capable of adsorbing potassium far in excesses of the amount which is normally applied in a fertilizer treatment for potatoes. The results show that potassium was adsorbed to a slightly greater degree from potassium sulfate than from potassium chloride. When potassium chloride and sodium chloride were mixed in the proportions found in manure salts (33:40), about the same amount of potassium was adsorbed per gram of soil as in the case where potassium sulfate was used, and slightly more than in the case where potassium chloride was used alone. These results indicate that undoubtedly the sodium chloride in

TABLE 2
Adsorption of potassium from 1 liter of solution by 200 gm. soil

SOLUTION	LEACHED	RETAINED	K ADDED	K IN LEACHING	K ADSORBED	WEIGHT K ADSORBED PER GRAM SOIL	pH LEACHING	CONDUCTIVITY OF (X 10 ⁻⁴) LEACHING
	cc.	cc.	gm.	gm.	gm.	gm.		
0.1 <i>N</i> KCl.....	940	60	3.9	0.9063	2.9937	0.0149	7.2	108.11
0.1 <i>N</i> K ₂ SO ₄	945	55	3.9	0.5627	3.3373	0.0166	7.0	180.97
0.1 <i>N</i> KCl + NaCl (Ratio (33:40)).....	945	55	3.9	0.5594	3.3406	0.0167	6.8	249.51

manure salts had little effect on the adsorption of potassium from potassium chloride in this soil. It would seem unlikely, then, that the potassium applied in manure salts under field conditions should penetrate to a greater depth in the soil and be removed from the feeding area of the potato plant. In this connection, the lower yields of potatoes reported elsewhere (12), where manure salts were compared with muriate and sulfate of potash, cannot be explained on this basis.

The reactions of the leachings are interesting since in only one case, where sodium chloride was added to a solution of potassium chloride, was the hydrogen ion concentration increased. This increased acidity may have been caused by a selective adsorption of the cations (3). In table 3 is shown the replacement of potassium in treated and untreated soil by a solution of 0.05 *N* HCl.

An inspection of table 3 reveals the fact that the potassium adsorbed by the soil from a solution of potassium sulfate is held more tightly than potassium adsorbed from a solution of potassium chloride. When potassium sulfate was

used, only 1.73 per cent of the adsorbed potassium could be replaced at the first leaching; at the second leaching, 0.41 per cent could still be replaced. However, for the potassium chloride solution, 2.45 per cent of the adsorbed potassium could be replaced at the first leaching and only a trace at the second leaching. The presence of sodium chloride apparently did not alter the amount of potassium replaceable.

It may also be seen from table 3 that only a trace of potassium was replaced when untreated air-dry soil was leached with a liter of 0.05 N HCl. For this reason no allowance was made for the replaceable potassium of the untreated

TABLE 3
Replacement of adsorbed K in 200 gm. treated and untreated soil by 0.05 N HCl

TREATMENT	LEACHED	K LEACHED	K ADSORBED	ADSORBED K REPLACE- ABLE	CONDUC- TIVITY $\times 10^{-4}$	pH
	cc.	gm.	gm.	per cent		
<i>Soil previously treated with 0.1 N KCl</i>						
1st leaching.....	500	0.0720	2.9937	2.45	57.00	2.5
2nd leaching.....	500	Trace	Trace	Trace	74.33	1.8
<i>Soil previously treated with 0.1 N K₂SO₄</i>						
1st leaching.....	500	0.05785	3.3373	1.73	43.77	2.7
2nd leaching.....	500	0.01612	3.27945	0.41	46.44	2.0
<i>Soil previously treated with 0.1 N KCl + NaCl</i>						
1st leaching.....	500	0.0689	3.3406	2.06	53.75	2.8
2nd leaching.....	500	Trace	Trace	Trace	43.14	2.1
<i>Untreated air-dry soil</i>						
1st leaching.....	500	Trace	27.63	2.8
2nd leaching.....	450	Trace	56.54	2.0

soil, in calculating the results in tables 2 and 3. For all treatments, the amount of potassium adsorbed by the soil was so large in comparison to that which was replaceable in the untreated soil, that the latter was negligible.

An examination of the conductivity measurements shows that there was an increase between the first and second leachings in every case but one. Further, it will be noted that in each case this increase was characterized by an increase in acidity, as shown by the pH values. Evidently some of the hydrogen ions in the first HCl leaching were used in replacing the adsorbed bases, as indicated by the percentage of potassium replaced in the first and second leachings. At the second leaching, more of the hydrogen ions passed through the soil and therefore the increased conductivity in this case was undoubtedly due to the

fast-moving hydrogen ions rather than to an increase in salt content. In the 0.05 *N* HCl solutions used the pH ranged from 1.6 to 1.8, the solutions being made only to approximate strength.

In an experiment of this kind it is not to be expected that equilibrium was reached between the soil and the leaching solutions. The duration of the leachings was entirely too short to permit equilibrium to be accomplished. Moreover, under field conditions it is very unlikely that equilibrium would ever be reached on account of the dynamic nature of the soil and the soil solution. It is because of this fact that it seemed justifiable to carry the problem into the laboratory under somewhat controlled conditions, and to use quantities of potassium salts considerably greater than those actually used in the field. Even at best, such experiments can only serve to indicate in a general way the adsorption that may be expected under field conditions.

EFFECT OF POTASSIUM MATERIALS ON NITRIFICATION

The small yields of potatoes that have been obtained where a fertilizer deficient in nitrogen was used in the Snow Hill experiments (12), establishes beyond a doubt the fact that nitrogen is a limiting factor in potato production on Norfolk sandy loam soil. Not only is it evident that the fertilizer used must be high in nitrogen, but it also seems necessary to supply part of the nitrogen from organic materials, in order to get the highest yields. Consequently, a study of the efficiency of nitrogenous fertilizers, in this case, may be extended to include the materials supplying phosphorus and potassium, in so far as they may affect the rate and accumulation of nitrates in the soil.

Phosphorus additions as a rule stimulate the bacterial activities in soil, but nearly all of the potassium salts very soon become toxic to bacterial action in soil when present in large amounts. The low-grade potassium salts are of especial significance in this respect, probably on account of their high sodium content.

Greaves (10) found potassium chloride stimulating to nitrification at low concentrations in the soil but becoming toxic as the concentration was increased. Potassium sulfate was found toxic at 6 p.p.m. in soil but the toxicity in this case was slow to increase as the salt content was increased. Lipman (13) has made perhaps the most extensive study of the effects of alkali salts on the activities of soil bacteria. In his studies, he found that sodium chloride was toxic to nitrifying organisms at a concentration of 0.1 per cent or less. Sodium chloride was found to be about as toxic for nitrifying as for ammonifying organisms. However, a stimulating effect on nitrification was found when sodium chloride was present in very small amounts. In a later publication, Lipman and Sharp (14) found that nitrogen-fixing organisms were more tolerant to sodium chloride than either the nitrifying or ammonifying organisms. Brown and Hitchcock (2), Gibbs, Batchelor, and Magnuson (9), Patterson and Scott (19), and Lipman (15) all reported a decrease in nitrification in soil when sodium chloride was present in high concentrations.

In order to study the relative effects of potassium chloride, potassium sulfate, and manure salts on the rate and accumulation of nitrates resulting from the nitrification of sulfate of ammonia, dried ground fish, and packing house tankage in Norfolk sandy loam, a rather extensive laboratory experiment was made.

METHODS AND PLAN OF EXPERIMENT

Commercial fertilizer materials were used to supply the nitrogen and potassium in the fertilizer mixtures, and for the phosphorus, 16 per cent superphosphate was used, making no allowance for the phosphorus contained in the organic materials. Analyses of the nitrogen and potassium materials are given in table 4.

The experiment was divided into three series according to the source of nitrogen used in the fertilizer mixture. In series I, dried ground fish was used as the only source of nitrogen supplying the equivalent of seven units of ammonia; in the same manner, packing house tankage was used in series II; and sulfate of ammonia in series III. In each series, equivalent amounts of

TABLE 4
Analyses of fertilizer materials used

	NH ₃	K ₂ O	NaCl
	per cent	per cent	per cent
Sulfate of ammonia.....	25.0		
Packing house tankage.....	7.2		
Dried ground fish.....	11.8		
Potassium chloride.....		50.2	14.0
Potassium sulfate.....		49.7	1.0
Manure salts.....		20.8	43.4

potassium were supplied from potassium chloride, potassium sulfate, and manure salts at three rates corresponding to 5, 8, and 10 units of potash. Six units of phosphoric acid were supplied in each case from superphosphate. By this arrangement, the source and amount of nitrogen and phosphorus remained constant throughout each series, and potassium varied within each series both as to source and amount.

The fertilizer mixtures were thoroughly mixed with surface soil taken from the Snow Hill experimental plots at the rate of 6 gm. per 2000 gm. of air-dry soil. This rate of treatment amounted to 345.9 mgm. of nitrogen and corresponded to a row application of 2000 pounds of fertilizer per acre analyzing 7 per cent ammonia. This is the customary fertilizer application made for potatoes at Snow Hill. After each treatment was made, the soil was placed in half-gallon glazed pots and removed to the greenhouse. Sufficient distilled water was added to bring the moisture content to 60 per cent of saturation. The combined weights of soil and pots were recorded and constant moisture conditions were maintained by additions of distilled water to weight at frequent

intervals. The temperature was recorded in the greenhouse during the experiment but was not controlled.

Immediately after moisture was added, a 70-gm. sample of the soil for the entire depth in each pot was taken with a brass tube. These samples were dried over night at 55°C. to check bacterial action. The nitrate content of each sample was determined by the phenoldisulfonic acid method as modified by Harper (11). This method was used throughout for all nitrate determinations, 50 gm. of soil being extracted with 250 cc. of distilled water for the determination. The hydrogen-ion concentration was determined electrometrically as in the previous experiments. Samples were taken every 20

TABLE 5

Effect of different amounts and different sources of potassium on nitrification of Dried Ground Fish in a complete fertilizer

Parts per million nitrate-nitrogen in air-dry soil*

SOURCE OF POTASSIUM	EQUIVALENT ANALYSIS	DECEM-	JANUARY	JANUARY	FEBRUARY	MARCH 4	MARCH 24	CONDUCTIVITY $\times 10^{-4}$
		BER 15	4	24	13	80 days	100 days	
Potassium chloride.....	7-6-5	3.5 6.5	2.1 6.7	50.4 6.2	140.8 5.2	109.0 5.3	109.6 4.9	4.8
Potassium chloride.....	7-6-8	3.5 6.6	3.6 6.7	34.7 6.3	126.6 5.3	113.2 5.1	133.3 5.0	5.0
Potassium chloride.....	7-6-10	3.5 6.5	3.4 6.5	13.2 6.2	89.8 5.6	115.4 5.2	109.9 5.0	6.6
Potassium sulfate.....	7-6-5	3.5 6.5	3.7 6.7	71.4 6.1	125.3 5.3	123.5 5.1	134.7 5.0	4.6
Potassium sulfate.....	7-6-8	3.5 6.8	3.5 6.8	60.8 5.9	116.3 5.5	114.0 5.1	99.2 5.0	4.6
Potassium sulfate.....	7-6-10	3.5 6.6	3.9 6.6	60.3 5.8	124.5 5.2	132.1 5.1	148.1 4.9	4.8
Manure salts.....	7-6-5	3.5 6.4	3.3 6.7	33.6 6.0	127.2 5.3	106.8 5.1	133.3 5.0	4.9
Manure salts.....	7-6-8	3.5 6.5	3.5 6.7	29.7 6.3	81.1 5.5	113.2 5.0	105.8 5.0	7.3
Manure salts.....	7-6-10	3.5 6.0	3.3 6.8	12.2 6.1	67.7 5.6	88.2 5.3	144.9 4.9	8.2
Control.....	7-6-0	3.5 6.7	7.3 6.3	88.8 5.9	109.9 5.3	72.2 5.2	100.0 4.5	4.1
Mean temperature, °F..			45.7	48.8	49.6	55.5	52.9	

* The average for all the determinations is given.

days for 100 days, and both nitrate and hydrogen-ion determinations were made on each sample. At the end of the experiment, conductivity measurements were made on each sample at 21°C. on a 1-5 extraction of each soil after being shaken for 2 hours. The total nitrates in parts per million of air-dry soil, the pH for each sample, and the conductivity results at the final period, are shown for each series in tables 5, 6, and 7.

DISCUSSION OF RESULTS

Series I

An examination of table 5 shows a marked reduction in the rate of nitrification of dried ground fish in every case, up to 40 days, where potassium materials

were added. At these periods, the nitrification of fish was greatest where potassium sulfate was applied in the lowest concentration, and smallest where manure salts were applied in the highest concentration. In almost every case, the relative nitrate accumulation up to 60 days seemed to decrease as the rate of potassium salts was increased. After 60 days, the rate of nitrification decreased where the most nitrates had accumulated and increased where a smaller amount of nitrates had accumulated. In some cases an actual loss of nitrate took place, probably due to the utilization of nitrates by the nitrate-assimilating organisms. As a consequence, the total nitrate accumulation at the end of the experiment was about the same in almost every case. A comparison of the reduction in rates of nitrification, as affected by the three

TABLE 6

Effect of different amounts and different sources of potassium on nitrification of Packing House Tankage in a complete fertilizer

Parts per million nitrate-nitrogen in air-dry soil*

SOURCE OF POTASSIUM	EQUIVALENT ANALYSIS	DECEMBER 15		JANUARY 4		JANUARY 24		FEBRUARY 13		MARCH 4		MARCH 24		CONDUCTIVITY $\times 10^{-4}$	
		0 days		20 days		40 days		60 days		80 days		100 days			
		days	pH	days	pH	days	pH	days	pH	days	pH	days	pH		
Potassium chloride.....	7-6-5	4.1	6.1	11.4	6.4	46.7	5.6	72.6	5.3	114.0	4.9	105.0	4.8	5.7	
Potassium chloride.....	7-6-8	4.1	6.0	11.3	6.2	40.4	5.5	66.2	5.0	69.3	5.0	120.5	4.8	6.3	
Potassium chloride.....	7-6-10	4.1	6.5	11.4	6.0	28.5	5.6	44.7	5.2	43.1	5.1	128.7	4.8	7.3	
Potassium sulfate.....	7-6-5	4.1	6.0	16.2	6.4	43.2	5.3	109.1	4.9	101.0	4.8	143.4	4.6	6.4	
Potassium sulfate.....	7-6-8	4.1	6.4	16.9	5.9	55.5	5.0	101.7	4.8	86.9	4.7	98.0	4.6	6.0	
Potassium sulfate.....	7-6-10	4.1	6.4	17.5	5.7	36.4	5.7	81.0	5.4	79.5	5.1	117.6	4.7	6.5	
Manure salts.....	7-6-5	4.1	6.0	11.0	6.4	20.2	5.7	107.1	5.0	76.9	5.1	76.5	4.9	7.4	
Manure salts.....	7-6-8	4.1	6.2	10.1	5.9	27.3	5.2	63.3	5.4	64.2	5.0	75.0	4.8	9.2	
Manure salts.....	7-6-10	4.1	6.0	8.6	6.0	20.5	5.9	27.0	5.2	56.3	5.4	54.0	4.9	9.0	
Control.....	7-6-0	4.1	6.6	21.2	5.9	40.7	5.6	86.7	4.7	110.7	4.5	95.2	4.9	5.7	

* The average for all determinations is given.

potassium materials used, shows manure salts to have the greatest effect, followed by potassium chloride and potassium sulfate in the order named.

The hydrogen-ion concentration did not seem to be a controlling factor in the nitrification of dried ground fish, even though there was a gradual increase in acidity throughout the experiment. The pH was remarkably constant for any one sampling, regardless of the source of potassium used. It may be noticed from the data in table 5 that the pH of the control was approximately the same as that of the potassium-treated soils at every sampling. This would indicate that the increase in acidity was caused by the action of microorganisms and not by the addition of potassium salts.

The conductivity measurements serve to indicate the relative salt content of the various soils. From table 5 it may be seen that there was a gradual increase

in conductivity at the end of the experiment which corresponded to the amounts of potassium materials applied at the beginning. The conductivity was especially high in the case of manure salts, indicating a high salt content where this material was used. It may also be noted from table 5 that the accumulation of nitrates, after 60 days, was inversely proportional to the conductivity of the samples at the end of the experiment.

Series II

As shown in table 6 the nitrification of packing house tankage was very similar to that obtained in series I where dried ground fish was used as the source of nitrogen. However, an examination of the data given in table 6

TABLE 7

Effect of different amounts and different sources of potassium on nitrification of sulfate of ammonia in a complete fertilizer

Parts per million nitrate-nitrogen in air-dry soil*

SOURCE OF POTASSIUM	EQUIVALENT ANALYSIS	DECEMBER 15		JANUARY 4		JANUARY 24		FEBRUARY 13		MARCH 4		MARCH 24		CONDUCTIVITY X 10 ⁻⁴
		0 days	pH	20 days	pH	40 days	pH	60 days	pH	80 days	pH	100 days	pH	
Potassium chloride.....	7-6-5	3.2	6.0	14.0	5.4	27.1	5.7	35.7	5.0	71.6	5.2	89.5	4.7	6.5
Potassium chloride.....	7-6-8	3.2	6.0	10.2	5.7	28.0	5.6	46.5	5.2	70.6	4.9	80.9	4.8	6.9
Potassium chloride.....	7-6-10	3.2	6.2	14.5	5.4	23.4	5.7	40.9	5.1	37.3	5.3	58.8	5.0	9.2
Potassium sulfate.....	7-6-5	3.2	5.9	19.2	5.6	47.0	5.5	46.9	5.2	66.7	4.9	105.3	4.5	6.3
Potassium sulfate.....	7-6-8	3.2	5.9	11.6	5.5	35.6	5.4	51.0	5.0	66.5	5.0	84.5	4.5	6.9
Potassium sulfate.....	7-6-10	3.2	6.4	19.2	5.6	40.8	5.4	61.5	4.8	84.0	4.7	101.7	4.7	6.9
Manure salts.....	7-6-5	3.2	6.1	13.0	5.3	30.6	5.3	54.0	5.0	62.2	5.0	63.8	4.8	7.4
Manure salts.....	7-6-8	3.2	5.6	9.4	5.7	22.4	5.7	36.7	5.2	38.1	5.0	59.4	5.1	8.5
Manure salts.....	7-6-10	3.2	6.3	9.0	5.6	18.9	5.6	33.5	5.1	34.4	5.4	49.0	4.7	10.1
Control.....	7-6-0	3.2	6.2	14.4	5.4	37.0	5.4	68.8	4.9	92.8	4.7	72.3	4.6	5.9

* The average for all determinations is given.

reveals some rather striking differences where manure salts were used. The rate of nitrification and the accumulation of nitrates in this case were decidedly less than in series I. Decreased nitrification with increasing applications of potassium was noticeable for all three potassium materials after 80 days, and when manure salts were used, a noticeable decrease was obtained even at the end of the experiment. In this series, as in series I, potassium sulfate, and to a lesser degree potassium chloride, at the lowest concentrations, showed an increased rate of nitrification over that obtained in the control.

No significant variations occurred in the hydrogen-ion concentrations of the successive samples in series II. The increase in acidity was gradual, as in series I, but the final pH was lower in most cases.

In all cases but two, measurements after 100 days showed a corresponding increase in conductivity with the rate of potassium applied at the beginning. The conductivity was highest and the accumulation of nitrates lowest, where manure salts were used. The accumulation of nitrates, up to 80 days, in every case was noticeably less as the conductivity increased.

Series III

The data obtained from the nitrification of sulfate of ammonia as affected by the various potassium materials are shown in table 7. The results show that both the rate of nitrification and the accumulation of nitrates were greater where potassium sulfate was used at all three concentrations, than where potassium chloride was used. A slight stimulating effect in the nitrification of sulfate of ammonia was evidenced by potassium sulfate after 20 and 40 days. In every case both the rate and accumulation of nitrates for the control were greater than where manure salts were used. The highest application of manure salts was very toxic to nitrification.

The initial and final pH of the samples in this series were, in the majority of cases, lower than those found in series I and II. This increased acidity was undoubtedly the result of acid formation during the nitrification of the sulfate of ammonia as pointed out by Waksman (26).

In series III the conductivity measurements again increased as the nitrate accumulation decreased. This was especially noticeable where manure salts were used. Nitrate accumulation was lowest for the entire series in every case where equivalent amounts of potassium were supplied by manure salts.

General discussion of results

From the results obtained in series I, II, and III it is evident that manure salts inhibited the nitrification of dried ground fish, packing house tankage, and sulfate of ammonia, when used as the only source of potassium in complete fertilizers containing 5, 8, and 10 units of potash. The toxic effect of the manure salts was more evident with increasing amounts, but even at the lowest rate, the nitrification of the nitrogenous materials with few exceptions, was less than where potassium chloride or potassium sulfate replaced this material in the mixture. It would seem from the conductivity measurements that this toxic effect was caused merely by an increase in total salt content. However, a careful examination of the data will show that this is not the case. In several instances nitrification was less where manure salts were used, than where potassium chloride or potassium sulfate was used, yet the total salt content of the soil containing manure salts, as indicated by conductivity, was lower than that of the soil containing the other potassium materials. It would seem that the toxic effect of manure salts is caused by the presence of sodium chloride. In this connection, Greaves (10) showed that in amounts exceeding 460 p.p.m. of sodium in the soil, sodium chloride became toxic to nitrification. He

attributed the toxic effect of sodium chloride to a physiological influence which it exerts upon the protoplasm of the organisms and not to a direct osmotic effect. Other workers, Lipman (13, 15), Patterson and Scott (19), Brown and Hitchcock (2), and Gibbs, Batchelor, and Magnuson (9) found that sodium chloride in concentrations of from 0.1 to 0.2 per cent was distinctly toxic to nitrifying organisms.

According to the analysis of manure salts given in table 4, this material contained 43.0 per cent sodium chloride. At the three rates used in this experiment, this would mean that sodium was applied with manure salts at the rate of 305,500, and 610 p.p.m. It is evident that the toxic limits for nitrification in the presence of sodium according to Greaves (10) was exceeded in every case where manure salts were used. The fact that small amounts of sodium chloride have been found to have a stimulating effect upon nitrification (1, 2), may account in part for the general increase in nitrate accumulations where potassium chloride and potassium sulfate were used. It may be seen from table 4 that both these materials contain a relatively small amount of sodium chloride. It is also possible that nitrification may have been stimulated somewhat by the potassium added, as it will be seen from the analysis in table I, that the soil was extremely deficient in this element.

From the foregoing experiments it is evident that the nitrogen and potassium fertilizer problems concerning the production of potatoes on Norfolk sandy loam are not distinctly separate. The experimental date presented show that the material used as a source of potassium may affect nitrification in the soil and thus influence the rate and accumulation of nitrates from nitrogenous materials. Manure salts, because of their large sodium chloride content, appear to be very toxic to nitrifying organisms when used in large amounts. The extent to which this material will reduce nitrification under field conditions is probably dependent upon the rate of application, amount of rainfall, and the soil. However, in field trials with potatoes on Norfolk sandy loam, it has not proved as satisfactory as either muriate or sulfate of potash.

CONCLUSIONS

1. Samples of Norfolk sandy loam soil adsorbed considerable amounts of potassium when leached with 0.1 *N* solutions of potassium salts.
2. The addition of sodium chloride to a solution of potassium chloride, in the proportions found in manure salts, did not reduce the amount of potassium adsorbed by the soil.
3. Potassium sulfate was adsorbed to a slightly greater degree than potassium chloride.
4. The potassium adsorbed from a solution of potassium chloride was replaced by dilute acid more rapidly than the potassium adsorbed from a potassium sulfate solution. The addition of sodium chloride did not affect the replacement of the potassium adsorbed from potassium chloride.
5. The nitrification of dried ground fish, packing house tankage, and sulfate

of ammonia was inhibited when manure salts were used as the only source of potassium in complete fertilizer mixture.

6. A slight stimulating effect on nitrification was obtained when potassium sulfate was used.

7. In general nitrification decreased as the concentration of the potassium materials increased, but the decrease was greatest where manure salts were used.

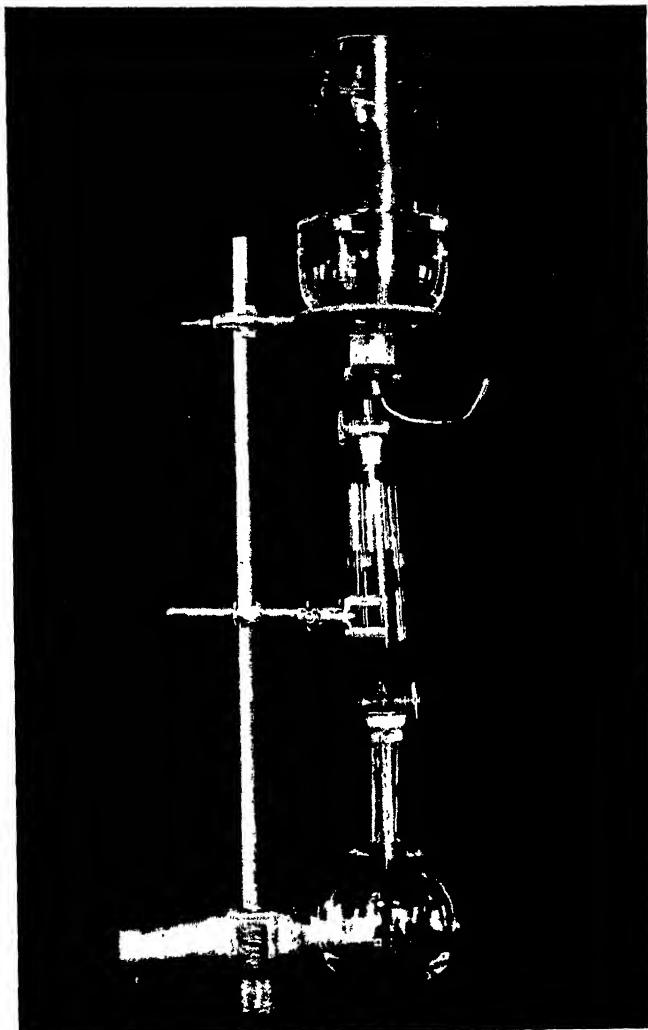
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PLATE 1

LEACHING APPARATUS USED FOR LEACHING SOIL WITH SOLUTIONS OF POTASSIUM SALTS AND
0.05*N* HCl



DISTRIBUTION OF NITRATES IN THREE LAYERS OF FALLOW SOIL¹

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The distribution of nitrates among three layers of fallow soil was studied for the summer season of 1926. The experiment was also designed to study the magnitude of economic losses by the action of leaching rains on large spring applications of easily nitrifiable fertilizer nitrogen.

PROCEDURE

Fertilizer chemicals equivalent to a ton per acre of a 6-8-6 fertilizer were thoroughly mixed with the top 7 inches of Merrimac silt loam on a $\frac{1}{5}$ -acre area. The 100 pounds of nitrogen applied were obtained equally from nitrate of soda, sulfate of ammonia, and high-grade tankage. The area chosen was a seldom used 20-foot roadway between two tiers of the permanent plats of this station. Although level in itself, the plat was bordered by a slight slope near one end that allowed sufficient run-off so that the larger rains did not exert a full leaching effect. The soil was plowed in the spring, plowed and rolled at midsummer, and received sufficient cultivation to prevent weed growth.

At frequent intervals samples were taken to represent three soil layers; namely, the surface 7 inches, the second 7 inches, and the 10-inch layer below the fourteenth inch. Thus, the three layers included the 2 feet of soil lying above a distinct profile of compact gravel. Twelve borings were composited to represent each layer. To prevent changes from taking place, nitrates and soil moistures were determined immediately after removal of the samples to the laboratory. On July 26, the pH value by the quinhydrone electrode was 5.5 for each of the three layers.

Acre weights of the three soil levels were calculated from the weight of a column of soil 10 inches in diameter, removed to the designated depths by means of a steel cylinder. Nitrates, determined in duplicate by the well-known phenoldisulfonic acid method, were calculated to pounds of nitric nitrogen in each soil layer. The results obtained are presented graphically in figure 1, together with a chart of the rainfall for the season, as measured with a rain gauge located 1 mile distant. Air and soil temperatures for the season have been reported previously (1).

¹ Contribution no. 368 of the station.

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DISCUSSION

While no exhaustive discussion of the results has been attempted, the general course of the fluctuations may be briefly interpreted. The first period, lasting until July 12, was one of steady gains in the surface level from nitrification of both fertilizer and soil nitrogen. Nitrate accumulations at the end of this period were the greatest found for the season; 193 pounds of nitric nitrogen being found in the 2-foot level, of which 112 pounds were in the surface layer. Losses from all three levels were caused by 1.4 inches of rain in five days; but

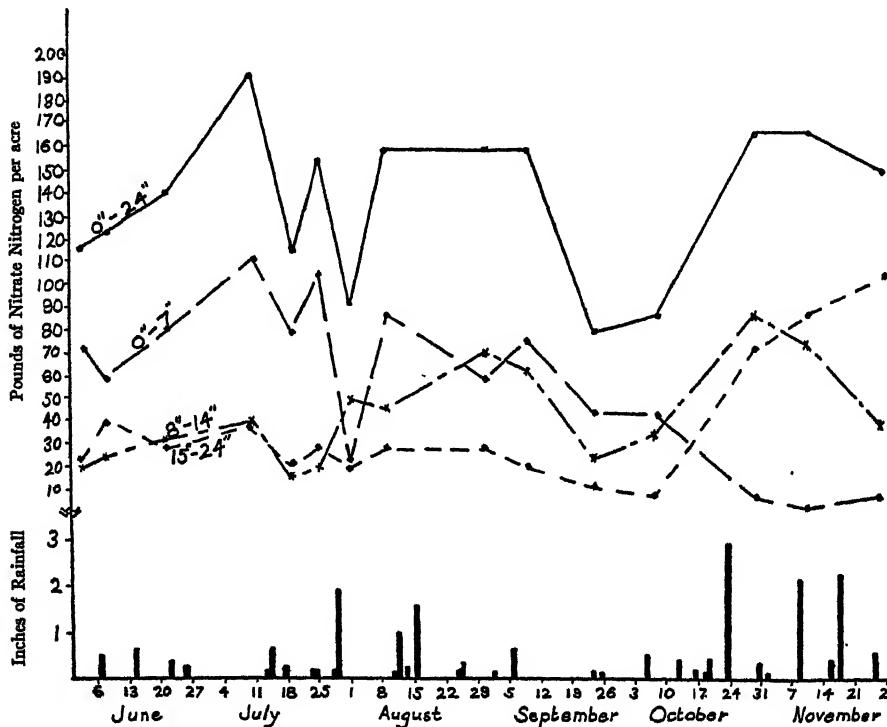


FIG. 1. DISTRIBUTION OF NITRATES IN THREE LAYERS OF FALLOW SOIL

were largely replaced, only to suffer more serious loss from leaching by the 2-inch rain of July 30.

At the time, this reduction of nitrate accumulations was considered critical, since but 23 pounds of nitric nitrogen remained in the surface soil, and it was believed that replacements from nitrification must have been exhausted. This belief was strengthened by the results of a laboratory nitrification test conducted on the samples of soil that were taken after the rain. Portions of soil from each level were incubated, some at room temperature and others at 35°C., from August 2 to 10, when the field soil was next sampled. Moistures were

maintained at the relatively high amounts found in the soils when sampled. During the incubation period the portions taken from the surface soil gained at the rate of 12 pounds of nitric nitrogen per acre at both temperatures, but no significant change was noted for the subsoils. Within the same time period, however, the recent nitrate losses from the three soils in the field were found to have been replaced. In addition, a gain was made equal to the slight gain from nitrification in the laboratory tests. Nitrates leached from the 2 feet of soil had been returned by a rise of the soil water as the surface soil dried under a hot August sun.

Between August 10 and 31, losses from the surface soil, caused by six days of persistent rains early in the period, appear to have been retained in the second 7-inch layer. It is probable that samples taken immediately after the rains would have shown more pronounced leaching.

No rain fell between September 9 and 23, but between these two dates occurred the most serious disappearance of nitrates that was noted for the season. The loss is attributed to the ascendancy of forms of microorganisms that assimilate nitrates, a common cause of nitrate disappearance. That this is a disappearance of nitrates and not an actual loss of nitrifiable nitrogen is shown strikingly by the rapid gains made by the soil as a whole before October 28. Autumn gains in nitrate accumulations have been demonstrated by other workers as reviewed by Russell (2), but the cause of the increased multiplication of ammonifying and nitrifying organisms is not entirely clear. The following possibilities have been suggested as causes: more advantageous moisture conditions from fall rains; decreasing numbers of nitrate-assimilating organisms due to the cooling of the soil; or a reduction in the numbers of soil protozoa that are believed to be inimical to nitrifiers. Whatever the cause of the increased nitrification, it is very probable that the protoplasm of the soil organisms that had assimilated the available nitrogen of the previous period, furnished the source of the nitrogen that was reconverted into nitrates.

A second point of interest is the fact that, although the soil as a whole gained in nitrate content in the late autumn, accumulations in the surface soil fell to a very low level. Under the influence of heavy rains, nitrate that was probably formed in the surface layer was leached rapidly into the subsoil. Had not the soil been somewhat more compact at the surface during this period than at the time of previous rains, there would have been less run-off and more pronounced leaching. The final determinations, November 26, show a downward movement of nitrates that presages the nearly complete disappearance of nitrates that occurs during the winter.

SUMMARY

For the entire season, there was little actual loss of easily nitrifiable nitrogen from the upper 2 feet of a fallow plat but vicissitudes of weather and the activities of the soil microorganisms caused decided temporary disappearances of

nitrates. Proportionate disappearances of nitrates under growing crops might well constitute critical deficiencies of available nitrogen. Nitrates moving downward after leaching rains, were often retained in the subsoil layers, and at such times the quantities there present were in excess of those remaining in the surface layer. Under midsummer conditions, nitrates leached from the upper soil layers were returned by the upward movement of soil water to replace that lost from the surface by evaporation.

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POTATO FERTILIZER EXPERIMENTS

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Experimental data dealing with potato fertilizers under Florida conditions are rather limited, yet the fertilizer cost is one of the most expensive items in connection with the production of this crop. Floyd and Ruprecht's (1) studies with potato fertilizers deal with the sources of phosphorus and the rate of potash fertilizers, and consequently have a limited application. No experimental results are available concerning nitrogen fertilization, although this is the most expensive nutrient. Furthermore, it is a common practice to use the plant nutrients from a combination of sources including organic and inorganic materials. This practice is probably unsound. Information concerning the rate of fertilizer application is only hypothetical. Some farmers claim that muriate of potash, although cheaper than sulfate, produces a lower yield and a poorer quality of potatoes. A few farmers make a practice of side-dressing the potato crop with various materials at the time the plants are from 4 to 6 inches high. Because of a lack of experimental data bearing on the aforementioned factors, the work reported in this paper was planned to throw as much light as possible upon these important questions.

EXPERIMENTAL.

In this experiment, two soil types both of which arose from costal plain deposits and occur in the costal plain soil area, were used. The soil types used are classified by the U. S. Department of Agriculture Bureau of Soils as Portsmouth loamy fine sand and Blanton fine sand. The Portsmouth loamy fine sand is a very dark brown to black loamy fine sand containing a high percentage of organic matter. This dark organic material extends to 15 to 24 inches then changes to a dark gray to gray fine sand, gradually becoming lighter with depth. Analysis showed 0.206 per cent nitrogen, 0.032 per cent phosphoric acid, 0.010 per cent potassium oxide, and a pH value of 5.8 to 6. The Blanton fine sand consists of 2 to 4 inches of a gray to dark gray fine sand, underlain by a yellowish-gray to grayish-white fine sand, 25 to 40 inches thick, resting upon a very light grayish-yellow to light gray fine sand. Analysis of this soil showed it to be considerably below the Portsmouth soil in organic matter, nitrogen, phosphorus, and potash.

¹ The author desires to express his thanks to the Barrett Company and to the Synthetic Nitrogen Products Corporation for supplying materials for this work.

Spaulding Rose No. 4 potatoes were used throughout and a ton of "standard" fertilizer, or its equivalent in plant-food, unless otherwise stated, made up according to the following formula was used to the acre:

	pounds
Nitrate of soda.....	110
Sulfate of ammonia.....	160
10 per cent blood and bone tankage.....	400
Goat manure.....	200
16 per cent acid phosphate.....	930
Sulfate of potash.....	200
	<hr/>
	2,000

The fertilizer was applied in the drill a few days before the potatoes were planted, and standard cultural practices were used throughout.

TABLE 1
The influence of rate of application of complete fertilizer on the yield of potatoes

BLOCK NUMBER	FERTILIZER TREATMENT
	lbs.
1	1,000 standard per acre
2	2,000 standard per acre
3	3,000 standard per acre
4	4,000 standard per acre

TABLE 2
Muriate vs. sulfate of potash as a source of potash for potatoes

BLOCK NUMBER	FERTILIZER TREATMENT
1	Sulphate of potash
2	Muriate of potash

Three sets of experiments were carried out, one on Blanton fine sand and the other two on Portsmouth loamy fine sand. One-fourth acre blocks were used throughout and the fertilizer treatments given in each set of experiments conformed to the outline in tables 1 to 5, unless otherwise stated.

Acid phosphate was used as the source of phosphorus throughout, and sulfate of potash as the source of potash except in the specific blocks where muriate of potash was used (table 2). In the portion of the experiment where top-dressers were used, 100 pounds of sulfate of ammonia or its equivalent in nitrogen was used to the acre.

The Blanton fine sand and one of the fields of the Portsmouth loamy fine sand soils used in this experiment were cropped to potatoes the previous spring and later were planted to cowpeas, which were turned under in the fall. Both these soils had been in cultivation the two years previous. The potatoes

were planted the second week in February, 1928, on the Blanton area and the preceding week on the Portsmouth loamy fine sand area. The other Portsmouth loamy fine sand area was virgin soil, not having been cultivated during

TABLE 3
The influence of different sources of nitrogen on the yield of potatoes

BLOCK NUMBER	SOURCE OF NITROGEN
1	Nitrate of soda
2	Sulfate of ammonia
3	10 per cent blood and bone tankage
4	Nitrate of soda, sulfate of ammonia, and 10 per cent blood and bone tankage ($\frac{1}{2}$ from each)
5	Nitrate of soda and sulfate of ammonia ($\frac{1}{2}$ from each)
6	Nitrate of soda and 10 per cent blood and bone tankage ($\frac{1}{2}$ from each)
7	Sulfate of ammonia and 10 per cent blood and bone tankage ($\frac{1}{2}$ from each)
8	Calcium nitrate
9	Nitrophoska
10	Standard
11	Ammo-Phos

TABLE 4
The influence of different materials as a top-dresser on yield of potatoes

BLOCK NUMBER	FERTILIZER USED FOR TOP-DRESSER
1	Nothing
2	Nitrate of soda
3	Calcium nitrate
4	Sulfate of ammonia
5	Sulfate of potash

TABLE 5
The influence of using the same source of nitrogen for top-dresser as that used in original fertilizer mixture on yield of potatoes

BLOCK NUMBER	SOURCE OF NITROGEN
1	Sulfate of ammonia
2	Nitrate of soda
3	Calcium nitrate

previous seasons. The potatoes on this area were planted during the second week in March. It was only on this field that the portion of the experiments contained in tables 4 and 5 was carried out.

RATE OF APPLYING COMPLETE FERTILIZER FOR POTATOES

In order to test experimentally the accuracy of the present practice of using 2000 pounds of fertilizer to the acre for potatoes, fertilizer was applied in varying amounts, ranging from 1000 to 4000 pounds to the acre. No check blocks on which fertilizer was omitted were included because it is common

TABLE 6

Influence of rate of applying complete fertilizer on yield of potatoes on Portsmouth loamy fine sand—potatoes planted first week in February, 1928

BLOCK NUMBER	AMOUNT OF FERTILIZER USED PER ACRE	YIELD IN BARRELS FOR $\frac{1}{2}$ ACRE	YIELD IN BARRELS PER ACRE
	lbs.		
1	1,000	12 $\frac{1}{2}$	49 $\frac{1}{2}$
2	2,000	14 $\frac{1}{2}$	58
3	3,000	14 $\frac{1}{2}$	57
4	4,000	13 $\frac{1}{2}$	54

TABLE 7

Influence of rate of applying complete fertilizer on yields of potatoes on Blanton fine sand

BLOCK NUMBER	AMOUNT OF FERTILIZER USED PER ACRE	YIELD IN BARRELS FOR $\frac{1}{2}$ ACRE	YIELD IN BARRELS FOR ONE ACRE
	lbs.		
1	1,000	10 $\frac{1}{2}$	40 $\frac{1}{2}$
2	2,000	15 $\frac{1}{2}$	62
3	3,000	13 $\frac{1}{2}$	55 $\frac{1}{2}$
4	4,000	15 $\frac{1}{2}$	62

TABLE 8

Influence of rate of applying complete fertilizer on yield of potatoes on Portsmouth loamy fine sand—potatoes planted second week in March, 1928

BLOCK NUMBER	AMOUNT OF FERTILIZER USED PER ACRE	YIELD IN BARRELS FOR $\frac{1}{2}$ ACRE BLOCK	YIELD IN BARRELS PER ACRE
	lbs.		
1	1,000	5 $\frac{1}{2}$	22 $\frac{1}{2}$
2	2,000	8	32
3	3,000	6 $\frac{1}{2}$	24 $\frac{1}{2}$
4	4,000	6 $\frac{1}{2}$	24 $\frac{1}{2}$

knowledge that without liberal fertilization it is useless to attempt to grow potatoes on many soil types in the state. The results of these experiments are contained in tables 6, 7, and 8.

The yields in table 6 show that the 2000-pound application produced the highest yield and also proved to be the most economical. The difference in the yields from the 2000-pound and 1000-pound application here should insure

a good rate of interest on the investment in the extra 1000 pounds of fertilizer. Quantities beyond 2000 pounds actually produced lower yields than that produced by the 2000 pounds.

An examination of the data in table 7 shows the results for Blanton fine sand to be similar to those in table 6 for the Portsmouth loamy fine sand.

There was a greater difference between the yields of the 1000- and 2000-pound applications on the Blanton soil than on the Portsmouth soil. This is to be expected, however, because of the characteristic difference between the two soil types.

The yields in table 8 are much lower than those in tables 6 and 7. This is accounted for in part by the fact that raw or virgin soil was used for this experiment and that considerable damage was done the crop by an unprecedented rainfall of 10.06 inches from April 10 to 27 inclusive. The potatoes were all but destroyed by this heavy rain. Each of these blocks also received a top dressing of 25 pounds of sulfate of ammonia when the plants were from 4 to 6 inches high.

Notwithstanding the handicaps placed on this experiment the results in general were in accord with those reported in tables 6 and 7.

MURIATE OF POTASH VS. SULFATE OF POTASH FOR POTATOES

Because of the lack of experimental data to substantiate the present practice of using sulfate of potash for potatoes instead of less expensive muriate of potash, a portion of the experiment was designed for that purpose. The results of this portion of the experiment are reported in table 9.

Blocks 1 and 2 of table 9 received standard potato fertilizer at the rate of 2000 pounds to the acre. Sulfate of potash was used as the source of potash for block 1, and muriate for block 2. Blocks 3 and 4 received Ammo-Phos potato fertilizer at the rate of 760 pounds to the acre; sulfate of potash was used as the source of potash for block 3; and muriate of potash for block 4. The 760 pounds of Ammo-Phos was equivalent in plant-food value to 2000 pounds of the standard potato fertilizer used in blocks 1 and 2.

It may be seen from the data in this table that the yields for the sulfate and muriate of potash blocks where the standard potato fertilizer was used were equal. The yields of the two Ammo-Phos blocks were considerably less than those of blocks 1 and 2 where the standard potato fertilizer was used, but the yield of block 4, in which muriate of potash was used as the source of potash, was 4 barrels per acre more than that of block 3, where sulfate of potash was used.

The fertilizer treatment of the four blocks in table 10 for Blanton soil was the same as that for corresponding block numbers for the Portsmouth soil reported in table 9. The yields for blocks 3 and 4, where Ammo-Phos was used as the basic fertilizer, were equal, showing that muriate of potash was equal to sulfate of potash as a source of potash for potatoes. The yield of

block 2, on which muriate of potash was used as the source of potash in the standard potato fertilizer, was considerably below that of block 1, in which sulfate of potash was used as the source of potash. This difference, however, may easily be accounted for by the fact that a small area in this block was occupied by a septic tank and by the fact that about half the length of one of the five rows in the block was set to satsuma orange trees after the experiment.

TABLE 9

Muriate of potash vs. sulphate of potash as a source of potash for potatoes on Portsmouth loamy fine sand—potatoes planted first week in February, 1928

BLOCK NUMBER	SOURCE OF POTASH	AMOUNT OF FERTILIZER USED PER ACRE	YIELD IN BARRELS FOR $\frac{1}{4}$ ACRE	YIELD IN BARRELS PER ACRE
		lbs.		
1	Sulfate of potash	2,000	14 $\frac{1}{2}$	58
2	Muriate of potash	2,000	14 $\frac{1}{2}$	58
3	Sulfate of potash	760	8 $\frac{1}{2}$	34
4	Muriate of potash	760	9 $\frac{1}{2}$	38

TABLE 10

Muriate of potash vs. sulfate of potash as a source of potash for potatoes on Blanton fine sand

BLOCK NUMBER	SOURCE OF POTASH	AMOUNT OF FERTILIZER USED PER ACRE	YIELD IN BARRELS FOR $\frac{1}{4}$ ACRE	YIELD IN BARRELS PER ACRE
		lbs.		
1	Sulfate of potash	2,000	15 $\frac{1}{2}$	62
2	Muriate of potash	2,000	13 $\frac{1}{2}$	52 $\frac{1}{2}$
3	Sulfate of potash	760	8 $\frac{1}{2}$	34 $\frac{1}{2}$
4	Muriate of potash	760	8 $\frac{1}{2}$	34 $\frac{1}{2}$

TABLE 11

Muriate of potash vs. sulfate of potash as a source of potash for potatoes on Portsmouth loamy fine sand—potatoes planted second week in March

BLOCK NUMBER	SOURCE OF POTASH	AMOUNT OF FERTILIZER USED PER ACRE	YIELD IN BARRELS FOR $\frac{1}{4}$ ACRE	YIELD IN BARRELS PER ACRE
		lbs.		
1	Sulfate of potash	2,000	8	32
2	Muriate of potash	2,000	6	24

was started. Unquestionably the yield of this block was affected by these factors.

Table 11 shows that the yields were extremely low. These results represent a portion of the late planted field which was all but destroyed by the heavy rainfall during April. The sulfate of potash block outyielded the muriate block by 8 barrels to the acre.

**THE INFLUENCE OF DIFFERENT SOURCES OF NITROGEN ON THE YIELD OF
POTATOES**

This portion of the experiment was planned for the purpose of determining the influence of some nitrogenous fertilizers as a source of nitrogen on the yield of potatoes. The results obtained are contained in tables 12, 13, and 14.

The data in table 12 show nitrate of soda, sulfate of ammonia, and 10 per cent blood and bone tankage to be of about equal value when used alone

TABLE 12

The influence of different sources of nitrogen on the yield of potatoes on Portsmouth loamy fine sand—potatoes planted first week in February, 1928

BLOCK NUMBER	SOURCE OF NITROGEN	YIELD IN BARRELS FOR $\frac{1}{4}$ ACRE	YIELD IN BARRELS PER ACRE
1	Nitrate of soda	16 $\frac{1}{2}$	67 $\frac{1}{2}$
2	Sulfate of ammonia	17	68
3	10 per cent blood and bone tankage	17	68
4	Nitrate of soda and sulfate of ammonia ($\frac{1}{2}$ from each)	16	64
5	Nitrate of soda and 10 per cent blood and bone tankage ($\frac{1}{2}$ from each)	13 $\frac{1}{2}$	53 $\frac{1}{2}$
6	Ammo-Phos	8 $\frac{1}{2}$	34
7	Standard	14 $\frac{1}{2}$	58

TABLE 13

Influence of different sources of nitrogen on the yield of potatoes on Blanton fine sand

BLOCK NUMBER	SOURCE OF NITROGEN	YIELD IN BARRELS FOR $\frac{1}{4}$ ACRE	YIELD IN BARRELS PER ACRE
1	Nitrate of soda	14 $\frac{1}{2}$	58 $\frac{1}{2}$
2	Sulfate of ammonia	13 $\frac{1}{2}$	53 $\frac{1}{2}$
3	10 per cent blood and bone tankage	14 $\frac{1}{2}$	58
4	Nitrate of soda and sulfate of ammonia ($\frac{1}{2}$ from each)	15 $\frac{1}{2}$	63 $\frac{1}{2}$
5	Nitrate of soda and 10 per cent blood and bone tankage ($\frac{1}{2}$ from each)	14 $\frac{1}{2}$	58
6	Ammo-Phos	8 $\frac{1}{2}$	34 $\frac{1}{2}$
7	Standard	15 $\frac{1}{2}$	62

as the sole source of nitrogen for potatoes. The yield per acre for nitrate of soda and sulfate of ammonia combined was slightly below that for each used alone, but was greater than those for nitrate of soda and 10 per cent blood and bone tankage combined and the standard respectively, and greater than that for Ammo-Phos.

Table 13 shows that the yields from nitrate of soda and 10 per cent Blood Bone Tankage used alone are about the same. The yield for the sulfate of ammonia block is slightly under that for the other two materials mentioned.

The yield for the nitrate of soda and sulfate of ammonia combined is the highest yield for any individual treatment, with that for the standard fertilizer running a close second. The yield for the nitrate of soda and 10 per cent blood and bone tankage block compares favorably with most of the other treatments. The Ammo-Phos yield, as with the Portsmouth loamy fine sand, is easily the lowest yield shown in the table.

The yields in table 14 are considerably lower on an average than those in the tables 12 and 13. This is partly because virgin soil was used for this portion of the experiment and the crop was severely damaged by the heavy rainfall previously reported for April. In addition to the fertilizer treatment indicated, each $\frac{1}{4}$ -acre block received 25 pounds of sulfate of ammonia as a top-dressing when the plants were from 4 to 6 inches high.

TABLE 14

Influence of different sources of nitrogen on the yield of potatoes on Portsmouth loamy fine sand—potatoes planted second week in March

BLOCK NUMBER	SOURCE OF NITROGEN	YIELD IN BARRELS PER $\frac{1}{4}$ ACRE	YIELD IN BARRELS PER ACRE
1	Nitrate of soda	12	50
2	Sulfate of ammonia	7	28
3	10 per cent blood and bone tankage	8 $\frac{1}{2}$	34 $\frac{1}{2}$
4	Nitrate of soda, sulfate of ammonia and 10 per cent blood and bone tankage ($\frac{1}{2}$ from each)	8 $\frac{1}{2}$	34 $\frac{1}{2}$
5	Nitrate of soda and sulfate of am- monia ($\frac{1}{2}$ from each)	9	36
6	Nitrate of soda and 10 per cent blood and bone tankage ($\frac{1}{2}$ from each)	9 $\frac{1}{2}$	37 $\frac{1}{2}$
7	Sulfate of ammonia and 10 per cent blood and bone tankage ($\frac{1}{2}$ from each)	8 $\frac{1}{2}$	33
8	Calcium nitrate	10	40
9	Nitrophoska	2 $\frac{1}{2}$	8 $\frac{1}{2}$
10	Ammo-Phos	2 $\frac{1}{2}$	8 $\frac{1}{2}$
11	Standard	8	32

The data in table 14 reveal the fact that nitrate of soda made the best showing, with calcium nitrate running second. Sulfate of ammonia, and 10 per cent blood and bone tankage were both considerably below the nitrate of soda block. The yield for the nitrate of soda and 10 per cent blood and bone tankage combinéd was slightly higher than those for the nitrate of soda and sulfate of ammonia combined, and for the nitrate of soda, sulfate of ammonia, and 10 per cent blood and bone tankage collectively. The yields for sulfate of ammonia and 10 per cent blood and bone tankage combined and for the standard were both somewhat below that of nitrate of soda and 10 per cent blood and bone tankage combined. The yield for the Nitrophoska and Ammo-Phos was easily the lowest of the group.

INFLUENCE OF DIFFERENT MATERIALS AS A TOP-DRESSER ON YIELD OF POTATOES

The portion of the experiment reported in table 15 was planned for the purpose of getting experimental data on the practice of top-dressing potatoes. For each acre 2000 pounds of the standard potato fertilizer was used. The nitrogenous top-dressing materials were used at the rate of the nitrogen equivalent of 100 pounds of sulfate of ammonia to the acre and the sulfate of potash 200 pounds. The top-dressing was applied April 8 or 9 just before the beginning of the heavy rains which fell from April 10 to 27 inclusive.

The figures in table 15 show that sulfate of ammonia and sulfate of potash produced slightly larger yields, and that nitrate of soda and calcium nitrate produced lower yields than block 1, on which no top-dresser was used. Sul-

TABLE 15
Influence of different materials as top-dressers on yield of potatoes

BLOCK NUMBER	TOP DRESSER	YIELD IN BARRELS PER $\frac{1}{4}$ ACRE	YIELD IN BARRELS PER ACRE
1	No top-dresser	7	28
2	Nitrate of soda	5 $\frac{1}{2}$	23 $\frac{1}{2}$
3	Calcium nitrate	5 $\frac{1}{2}$	21 $\frac{1}{2}$
4	Sulfate of ammonia	8	32
5	Sulfate of potash	8 $\frac{1}{2}$	34

TABLE 16
Influence of same material used for top-dresser as that used for source of nitrogen in the original fertilizer mixture on yield of potatoes

BLOCK NUMBER	FERTILIZER MATERIAL	YIELD IN BARRELS PER $\frac{1}{4}$ ACRE	YIELD IN BARRELS PER ACRE
1	Sulfate of ammonia	7	28
2	Nitrate of soda	5	20
3	Calcium nitrate	7	28

fate of potash produced the highest yield and calcium nitrate the lowest yield of all the treatments. The results from sulfate of ammonia and sulfate of potash reported in this table are in keeping with another similar experiment conducted on the same type of soil where 1 acre each was top-dressed with sulfate of ammonia and sulfate of potash with a yield of 50 barrels to the acre for the sulfate of ammonia and 64 for the sulfate of potash treated acres.

MATERIAL USED FOR TOP-DRESSER

The portion of the experiment reported in table 16 is really a continuation of that reported in table 15. In this case, however, the same source of nitrogen was used for the top-dresser as for the original fertilizer mixture applied.

The data in table 15 reveal the fact that the yields were also very low but they, too, were seriously effected by the heavy April rains.

DISCUSSION

The data presented in this paper show conclusively that the 2000-pound per acre application of a complete fertilizer was the most economical of the four applications made. The yield from the 2000-pound application was considerably above that for the corresponding 1000-pound application in each of the three experiments. It was also greater than that for the corresponding 3000-pound application in each case, but the difference was less pronounced than with the 1000-pound application. With one exception the same was true with the 4000-pound application. The 4000 pound application on Blanton fine sand was the same as that for the 2000 pound on the same soil.

There were no characteristic visible differences between the vegetative growth of the plants in the blocks receiving the different amounts of fertilizer during the growing season.

The results reported in tables 9, 10, and 11 indicate there is no decided advantage in favor of either muriate or sulfate of potash as a source of potash on the yield of potatoes. Both the sulfate and muriate of potash blocks, where the standard potato fertilizer was used, produced 58 barrels to the acre on the early planted Portsmouth loamy fine sand. Muriate, however, produced 4 barrels to the acre more than sulfate on the same soil when used in conjunction with Ammo-Phos. Sulfate of potash used in combination with the standard potato fertilizer produced $9\frac{1}{2}$ barrels to the acre more than muriate of potash used in the same manner on the Blanton fine sand. This difference, however, may easily be accounted for by the fact that a small area in this block was occupied by a septic tank and to the fact that about half the length of one of the five rows in the block was set to satsuma orange trees soon after the potatoes were planted. These two factors evidently influenced the yields to some extent. The yields for muriate and sulfate of potash were the same in the Ammo-Phos blocks of the same test.

Sulfate of potash produced 8 barrels to the acre more than muriate on the late planted Portsmouth loamy fine sand. Other experimental data at hand, not reported in this paper, show muriate of potash to be slightly superior to sulfate as a source of potash for potatoes.

Nitrate of soda, sulfate of ammonia, and 10 per cent blood and bone tankage used individually as the source of nitrogen in a complete fertilizer for potatoes on Portsmouth loamy fine sand and Blanton fine sand soils compared favorably with the standard potato fertilizer in their influence on the yield. The nitrogen in the standard potato fertilizer was supplied from nitrate of soda, sulfate of ammonia, 10 per cent blood and bone tankage, and goat manure. Each of the above mentioned nitrogenous materials when used individually produced about 10 barrels to the acre more than the standard material on the early planted Portsmouth loamy fine sand. On this same soil nitrate of soda and sulfate of ammonia in combination produced 6 barrels to the acre more than the standard, whereas nitrate of soda and 10 per cent blood

and bone tankage in combination produced $4\frac{2}{3}$ barrels per acre less than the standard.

On Blanton fine sand, nitrate of soda and tankage where used individually and nitrate of soda, sulfate of ammonia, and blood and bone tankage in the combinations reported, produced yields that compared favorably with that of the standard. These results indicate that our present practice of using for potatoes, nitrogen from several sources, including the expensive organic materials, may not be well founded.

The results with Ammo-Phos are as interesting as those discussed for the other materials. The yields for Ammo-Phos are a little more than half as large as the yields obtained by other materials. This material had a decidedly retarding influence on the germination and growth of the plants. All areas fertilized with this material were characterized by a poor stand. In addition to the results previously reported in this paper the yield on 11 acres of commercial potatoes fertilized with this material was nil.

The yields on the late planted Portsmouth loamy fine sand were not so large or consistent as similar yields on the other two experiments. This may be due in a large measure to the effect of the 10.06 inches of rain which fell from April 10 to 27 inclusive, however. Notwithstanding this fact there are several points worthy of mention.

The nitrate of soda block was easily the best yielding block in the test. Calcium nitrate which was second, yielded 10 barrels to the acre less than nitrate of soda. Several of the other combinations out-yielded the standard treatment. Nitrophoska and Ammo-Phos affected the plants in about the same peculiar manner and produced the same yield, which was only about one-fourth that of the next lowest yield.

The heavy April rains resulted in low yields for the top-dresser experiments. Sulfate of ammonia and sulfate of potash were the only two top-dressing materials used in combination with the standard potato fertilizer that resulted in increased yields over the block on which the top-dresser was omitted. This increase was 4 barrels to the acre for sulfate of ammonia and 6 for sulfate of potash. The sulfate of potash results obtained here are in keeping with similar results where these two materials were used as top-dressers on full acre blocks of Portsmouth loamy fine sand. Sulfate of ammonia produced 50 barrels to the acre compared with 64 for sulfate of potash. Nitrate of soda and calcium nitrate were negative in their results in this experiment. This may have been due in part to the fact that the heavy April rains started the day following the application of the top-dressing materials and that the more soluble materials were more easily leached from the soil.

Sulfate of ammonia and calcium nitrate produced the same yield when used as the source of nitrogen for both the original fertilizer and the top-dresser. Both these were superior to nitrate of soda in this respect.

CONCLUSIONS

The data reported in this paper seem to justify the following conclusions:

1. The 2,000-pound rate application of fertilizer was the most economical rate used.
2. Sulfate of potash has no decided advantage over muriate of potash as a source of potash on potato yield.
3. The present practice of supplying, in potato fertilizers, nitrogen from several sources, including expensive organic materials, may be ill founded.
4. Nitrate of soda, sulfate of ammonia, 10 per cent blood and bone tankage, and calcium nitrate when used singly and in the combinations reported, were about as satisfactory as sources of nitrogen for potatoes as the combination used in the standard potato fertilizer mixture.
5. Ammo-Phos was unsatisfactory as a source of nitrogen for potatoes.
6. Sulfate of potash and sulfate of ammonia increased potato yields when used as top-dressers.

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THE BUFFER METHOD AND THE DETERMINATION OF EX- CHANGEABLE HYDROGEN FOR ESTIMATING THE AMOUNTS OF LIME REQUIRED TO BRING SOILS TO DEFINITE pH VALUES¹

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Probably no phase of the problem of soil acidity has received more attention than has the study of methods for determining the amount of lime necessary to correct the acidity of the soil. It is not the purpose of this paper to discuss these methods for they have been studied and compared by a number of investigators (6, 9, 10). The results of these investigations show that the various methods often give widely different values. This is not surprising when one considers, as was pointed out by Christensen and Jensen (1), that the procedure, the reagents used, and the end point all vary. Thus, most of the methods are qualitative or only roughly quantitative; and although they have been of great value as a basis for making practical liming recommendations, there is need of a more accurate quantitative method that will give a measure of the amount of lime necessary to bring the soils to definite pH values.

Although it is recognized that we know only very incompletely what the range of pH for optimum growth of various plants is, yet there is considerable evidence for the belief that the optimum pH value for most crops is between pH 6.0 and 6.5. It is at least safe to say that most of the ordinary farm crops would not respond to liming on soils that already have a reaction of nearly pH 6.5. A laboratory method, therefore, that would enable soils workers to determine the amount of lime necessary to bring soils to pH 6.0, pH 6.5, or to any other pH value would be of considerable value. It would be especially valuable in making liming experiments.

In many experiments that have been conducted in the past to determine whether different crops respond to liming on various soils, there has been little attention paid to the amount of lime applied as related to the amounts necessary to bring the soils to definite reaction values. In some experiments the amounts of lime added were no doubt inadequate; in others an actual excess of lime was sometimes applied, in which cases there may have been injury to crops from liming. Such injurious effects of lime have been reported by a

¹ Published with the permission of the Director of the Alabama Agricultural Experiment Station.

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number of investigators (2, 8, 14). In a preliminary greenhouse liming experiment on sandy Coastal Plain soils conducted at this station it was found that only when the soils were limed above pH 7.0, or 6.5 in some cases, did injury occur. Any method, then, that would give the amounts of lime required to bring soils to definite pH values would not only be of great value as a basis for liming in lime experiments, but also for making practical lime recommendations especially on sandy soils where the amounts of lime necessary are usually small and where there is danger of overliming.

The titration or buffer curves express the pH of soil suspensions at equilibrium after the addition of base or acid. This method has been suggested by various investigators as means of determining the amount of lime necessary to bring a soil to neutrality or to definite pH values. Hissink (7), Crowther (4), and Christensen and Jensen (1), however, have all called attention to the fact that buffer curves determined in the laboratory do not give the actual figures for the amount of lime that must be added to a soil to bring it to a certain pH value. Christensen and Jensen (1) state,

Even when the best possible technical aid is at hand for making a laboratory determination of a soil's buffer effect on lime, it is by no means permissible—though often done—to apply directly the values found in such investigation to field soils; on the contrary there is every reason to believe that the same amount of lime causes a greater reaction change in a given quantity of soil when it is mixed with soil in suspension in retorts than when it is applied in the field in practical farming mixed with soil as more or less finely ground marl or lime

These last named authors conducted an investigation on eight Danish soils with the purpose of finding out the relationship between the buffer curves and the amounts of lime required in the field to bring soils to definite pH values. They found that the relation between these two values, which they term "liming factor," is about 3.0. In other words, it took three times as much lime in the field to bring a soil to a certain pH value as it did to bring the soil suspension to the same reaction in the laboratory. They do not consider in determining this value of 3.0, however, the very important question as to the possible movement of lime into the subsoil although they do recognize that such a downward movement of lime will influence the size of the "liming factor." Crowthers (5) has shown very conclusively that there is a considerable movement of lime into the subsoil, and he considers this as the main reason for a "liming factor." With the exception of the excellent but rather limited investigation of Christensen and Jensen, there has been no attempt to standardize the buffer method so that it could give accurate values for the amounts of lime necessary to bring soils to definite pH values.

The purposes of this investigation were as follows: 1. To work out a simple method for the determination of the titration or buffer curves of soils; 2. To determine the correlation between the buffer action of soils toward base as determined in the laboratory and the amounts of lime necessary to bring soils to definite pH values; 3. To determine the H-ion concentration of soils limed according to their content of exchangeable hydrogen.

METHOD FOR DETERMINING THE TITRATION OR BUFFER CURVES OF SOILS

Various methods have been used in determining the buffer or titration curves of soils. Some of these have been briefly reviewed in a recent publication by one of the authors (12). In the investigation reported, a very satisfactory method was developed for determining the buffer capacity of soils toward acid. This method involves the use of collodion sacks and the colorimetric method of determining H-ion concentration. The procedure is briefly as follows: 20-gm. samples of soil, the buffer capacity of which is to be determined, are placed in a series of 150-cc. collodion sacks, placed inside 150-cc. extraction flasks. One flask is left untreated, whereas various amounts of 0.1 N H_2SO_4 or 0.1 N $\text{Ba}(\text{OH})_2$, as the case may be, are added to the other sacks

TABLE 1

Time necessary for the establishment of equilibrium between $\text{Ba}(\text{OH})_2$ and the soil in suspension

TREATMENT 0.4 N $\text{Ba}(\text{OH})_2$ PER 20 GM. OF SOIL	H-ION CONCENTRATION AFTER VARIOUS PERIODS OF TIME					
	10 hours	1 day	2 days	3 days	4 days	7 days
cc.	pH	pH	pH	pH	pH	pH
<i>Norfolk sand</i>						
None	5.75	5.65	5.65	5.65	5.60	5.60
0.8	6.80	6.35	6.20	6.15	6.15	6.15
2.0	8.45	7.20	7.05	7.00	7.00	7.00
3.2	8.80+	7.60	7.55	7.45	7.45	7.45
<i>DeKalb fine sandy loam</i>						
None	5.75	5.80	5.80	5.80	5.80	5.80
1.2	7.15	6.60	6.55	6.50	6.40	6.30
2.0	8.60	7.00	6.80	6.75	6.75	6.65
3.2	8.80+	7.45	7.20	7.15	7.15	7.05
<i>Decatur silt loam</i>						
None	5.80	5.80	6.00	6.20	6.25	6.60
2.0	6.70	6.55	6.55	6.60	6.60	6.60
4.0	8.80	7.00	6.95	6.95	6.90	6.80
6.0	8.80	8.00	7.45	7.35	7.35	7.25

in increasing amounts. Distilled water is then added partly to the inside and partly to the outside of the sacks to bring the total volume of liquid to 100 cc. The necks of the sacks are then folded against the necks of the flasks; clean rubber stoppers are inserted; and the flasks are set aside and shaken five or six times a day until equilibrium is established. This requires three days. Then determinations are made on the clear diffusate by the colorimetric method.

The time necessary for equilibrium, and the kind of base to use are questions of considerable importance. Theoretically, it would seem preferable to use

$\text{Ca}(\text{OH})_2$ solution. Several investigators (7) (3) have shown, however, that $\text{Ca}(\text{OH})_2$ and $\text{Ba}(\text{OH})_2$ give the same results. NaOH , on the other hand, was found to give different values. It was decided, therefore, to use $\text{Ba}(\text{OH})_2$, since it is more commonly used as a laboratory reagent than is $\text{Ca}(\text{OH})_2$ because it can be made up in greater concentrations than the latter.

The data presented in table 1 show that between two and three days are necessary for equilibrium. This was confirmed by determinations on a large number of other soils. Three days, therefore, was considered as the standard for the procedure. The Decatur silt loam soil is included in this table because of the peculiar tendency of the untreated soil to get less acid with time. No other soil studied showed such a large change. This indicates the importance of having an untreated sample with each series.

This method has the advantage that a clear extract is always secured. Determination of the H-ion concentration, therefore, is made easily and quickly by the colorimetric method.

THE CORRELATION BETWEEN THE BUFFER ACTION OF SOILS TOWARD BASE AS DETERMINED IN THE LABORATORY AND THE AMOUNTS OF LIME IT TAKES TO BRING SOILS TO DEFINITE pH VALUES BY LIMING

As previously mentioned, several investigators (4, 1) have shown that a greater amount of lime must be added to field soils than to the soil suspension in the laboratory to bring a soil to definite pH value. This relation between the two amounts, called "liming factor" by Christensen and Jensen, can be calculated as follows:

$$\text{"Liming factor"} = \frac{\text{mgm. equiv. of lime per 100 gm. soil in field or greenhouse soil to bring it to } x \text{ pH value.}}{\text{mgm. equiv. of base per 100 gm. soil in soil suspension to bring soil to } x \text{ pH value,}}$$

where x may represent any pH value. If 20 gm. of soil and 0.1 *N* $\text{Ba}(\text{OH})_2$ are used in the buffer method in the laboratory, and we represent the amount of calcium carbonate added to field or greenhouse soils on the basis of tons per acre 2,000,000 pounds of soil, the equation can be represented as follows:

$$\text{"Liming factor"} = 4x \left\{ \frac{\text{T. per acre CaCO}_3 \text{ required to give } x \text{ pH value}}{\text{cc. 0.1N}\text{Ba}(\text{OH})_2 \text{ per 20 gm. soil in suspension to give } x \text{ pH value.}} \right\}$$

In these experiments the lime was applied to soils in pots or tumblers in the greenhouse rather than to field soils. This seemed preferable, since it is known that the downward movement of lime in the field varies from soil to soil. Therefore, unless the question of downward movement is also studied, the "liming factor" obtained in the field may apply only to the one soil studied.

By liming in pots where there is no loss by leaching and the amount of soil reacting with the lime is definitely known, it is possible to get at a much more accurate "liming factor."

The first part of the investigation was carried on with 58 sandy Coastal Plain soils that had been limed in pots in the greenhouse at the uniform rate of

TABLE 2

The "liming factor" or the relation between the H-ion concentration of soils treated with Ba(OH)₂ according to the buffer capacity method, and the reaction of soils limed at the rate of 1 ton per acre

SOIL NUMBER	SOIL TYPE	H-ION CONCENTRATION OF 1:5 SOIL WATER EXTRACTS					"LIMING FACTOR"	
		No treatment	Limed at rate of 1 ton per acre in pots and cropped	Treated with following amounts of 0.1 N Ba(OH) ₂ per 20 gm. of soil in suspension.				
				2.0 cc.	3.0 cc.	4.0 cc.		
564	Norfolk sand	pH	pH	pH	pH	pH	1.38	
565	Greenville sand	5.45	6.90	6.60	6.95	7.20	1.51	
566	Norfolk fine sand	5.50	6.70	6.45	6.85	7.00	1.43	
567	Greenville sand	5.40	6.85	6.45	6.95	7.15	1.63	
568	Greenville sand	5.65	6.60	6.40	6.85	7.15	1.38	
569	Greenville sand	5.15	6.80	6.40	6.85	7.00	1.58	
570	Greenville pebbly loam	4.85	5.65	5.50	5.70	5.95	1.33	
571	Greenville sandy loam	5.40	6.60	6.30	6.60	6.85	1.74	
572	Norfolk sandy loam	5.25	5.85	5.80	5.95	6.10	1.33	
573	Norfolk sandy loam	5.30	6.35	6.10	6.35	6.55	1.57	
574	Norfolk sandy loam	5.50	6.00	5.80	6.20	6.45	1.48	
575	Greenville loam	5.60	6.35	6.20	6.40	6.65	1.58	
576	Greenville sand	5.70	6.25	6.20	6.30	6.40	1.33	
577	Orangeburg very fine sandy loam	5.60	7.30	6.90	7.30	7.65	1.33	
578	Greenville sandy loam	5.65	6.85	6.55	6.85	6.95	1.60	
579	Ruston sand	5.65	6.75	6.40	6.75	7.05	1.33	
580	Orangeburg sandy loam	5.40	6.25	6.15	6.35	6.40	1.33	
581	Norfolk sand	5.55	6.35	6.20	6.35	6.55	1.40	
582	Kalmia very fine sand	5.60	7.40	7.20	7.40	7.60	1.33	
583	Greenville sand	5.40	6.30	6.10	6.40	6.50	1.33	
584	Norfolk sandy loam	5.60	6.95	6.70	6.90	7.20	1.27	
585	Orangeburg sandy loam	5.65	6.75	6.40	6.75	6.95	1.33	
586	Orangeburg sandy loam	5.65	7.15	6.90	7.15	7.40	1.33	
587	Norfolk fine sand	5.60	6.95	6.70	6.90	7.20		
588	Orangeburg fine sand	5.65	6.75	6.40	6.75	6.95		

1 ton of pure precipitated calcium carbonate per acre. The pots were limed in the fall of 1926 and melilotus was grown during the winter of 1926-27. After the removal of the crop, approximately 6 months after the lime had been applied, samples of the limed and unlimed soils of each series were taken and their pH value determined by the dialysis-colorimetric method previously

described (13). Determinations of the buffer action toward base were then made on the unlimed soils. The data for the first 25 soils are presented in table 2.

It will be noted that the soils vary in original reaction from pH 4.85 to pH 6.4, and that the reaction after liming varies from pH 5.85 to pH 7.4. In columns 5, 6, and 7 are given the pH values of the soils after the addition of 2, 3, and 4 cc. of 0.1 N Ba(OH)₂, respectively. From these data, curves were drawn plotting pH values against cc. of 0.1 N Ba(OH)₂ used. Since only one rate of liming was used in the pots, a second curve could not be drawn for each soil, but the amounts of Ba(OH)₂ required to bring the soil to the pH value it

TABLE 3

The "liming factor" of soils at different pH values, using the buffer method for determining titratable acidity in the laboratory

SOIL NUMBER	SOIL TYPE	H-ION CONCEN-TRATION	EX-CHANGE-ABLE HYDRO-GEN*	TOTAL EX-CHANGE CAPACI-TY*	"LIMING FACTOR" AT pH VALUES		H-ION CON-CENTRA-TION OF SOILS LIMED TO NEUTRALIZE EXCHANGE-ABLE HYDROGEN
					6.00	6.50	
372	Norfolk sand	pH	mgm. equiv.	mgm. equiv.			pH
373	Ruston sandy loam	5.80	0.80	1.57	1.41	1.42	6.58
375	Greenville sandy loam	5.60	1.07	2.12	1.52	1.33	6.20
376	Norfolk sandy loam	6.00	1.15	2.51	1.35†	6.58
377	Decatur silt loam	5.60	1.20	2.39	1.73	1.38	6.58
386	Decatur silt loam	5.50	3.90	8.22	1.43	1.54	6.70
518	Gray silt loam	6.00	4.00	7.83	1.80†	6.75
548	Black clay loam	4.45	8.18	8.18	1.78	1.67	6.20
559	Sandy muck	5.00	28.50	28.50	1.43	1.46	6.45
Average.....		4.40	10.40	10.40	1.31	1.21	6.40
					1.52	1.43	
							6.49

* Figures given refer to mgm. equiv. per 100 gm. of soil.

† Not included in average.

had after liming were interpolated from the buffer curve and compared with the amounts of lime added to the pots in the greenhouse.

It will be noted that the "liming factor" for the twenty-five soils varied from 1.27 to 1.74 and that the average of all factors is 1.43. The other thirty-three soils gave much the same values and were, therefore, not included in the table. The average factor for the fifty-eight soils was 1.42, and the extremes in the factor were 1.14 and 1.77. Thirty-five of the soils gave a deviation from the average of less than 0.10, whereas fifty-one gave a deviation of less than 0.20. This is regarded as a rather constant factor, especially when one considers that the determinations were not made in duplicate and that the calculations were made at widely different pH values with the different soils.

In another experiment nine soils of widely different pH values and total

exchange capacity were treated in tumblers with various definite amounts of precipitated calcium carbonate. They were brought to optimum moisture content and the tumblers were placed in a desk in the laboratory where evaporation was not excessive. Water was added to bring the soils back to the optimum moisture content at intervals of a few weeks. At the end of six months each sample was allowed to dry, was thoroughly mixed, and its pH value was determined. As with the soils previously discussed, buffer determinations were made on the untreated soil which had similarly been kept at the optimum moisture content for the preceding six months. The data secured from the buffer determinations and from the use of CaCO_3 in tumblers were plotted on

TABLE 4

The H-ion concentration and "liming factor" of soils limed in amounts equivalent to their respective amounts of exchangeable hydrogen

SOIL NUMBER	SOIL TYPE	LOCATION OF SOIL	EXCHANGEABLE HYDROGEN*	H-ION CONCENTRATION OF SOIL	H-ION CONCENTRATION OF LIMED SOIL AFTER			"LIMING FACTOR"
					2 months	4 months	6 months	
670	Black clay loam	Ill.	9.90	5.20	6.75	6.60	6.60	1.32
671	Gray silt loam	Ill.	7.20	4.50	6.40	6.25	6.35	1.60
672	Cecil sandy loam	S. C.	3.20	5.80	6.78	6.58	6.63	1.52
673	Brown silt loam	Miss.	0.90	6.48	6.95	6.83	6.83	1.80
674	Cecil clay loam	Ala.	2.50	6.00	7.00	6.80	6.80	1.67
675	Norfolk sandy loam	Ala.	1.39	5.65	6.55	6.48	6.53	1.55
676	Colby silt loam	Wis.	5.80	5.60	6.80	6.63	6.75	1.57
678	Cecil clay loam	Ala.	2.65	5.50	6.90	6.65	6.68	1.33
679	Miami silt loam	Wis.	3.80	5.80	6.80	6.65	6.68	1.58
680	Greenville fine sandy loam	Ala.	4.60	5.40	6.70	6.55	6.58	1.59
Average for all soils.....					6.76	6.60	6.64	1.55

* Expressed as mgm. equiv. per 100 gm. of soil.

graphs, pH values being used as abscissas, and the amount of $\text{Ba}(\text{OH})_2$ and CaCO_3 as ordinates. Calculations were then made of the "liming factor" at the pH values of 6.00, and 6.50 wherever possible. The data are presented in table 3.

In columns 6 and 7 are given the "liming factors" at pH 6.00 and 6.50, respectively. It will be noted, in the first place, that the average factor at pH 6.50 is 1.43 or very similar to the average factor for the fifty-eight soils already discussed. This average is only of the values for which figures are also given at pH 6.00. The average factor at pH 6.00 was found to be 1.52 or very similar to that obtained at 6.50.

The data in the last column of this table is discussed later in the paper.

In connection with the work for the latter part of this paper, the "liming factor" of ten other soils of widely different pH values and exchangeable hydrogen content was determined. These soils had been limed in the greenhouse with precipitated calcium carbonate in amounts equivalent to the exchangeable hydrogen present. The "liming factor" is calculated at a single pH value for each soil, which varied for the different soils between 6.25 and 6.83. The data are given in the last column of table 4. It will again be noted that the factors are quite consistent, giving an average of 1.55. Most of these soils are heavy in texture, and this fact is believed to explain the slightly higher average value obtained than that secured for the sandy Coastal Plain soils reported in table 2.

For all practical purposes the differences in the factors obtained with the 77 soils studied are of little if any significance. In applying the buffer method to the determination of the amount of lime necessary to bring soils to a definite pH value, the "liming factor" of 1.50 is recommended.

THE H-ION CONCENTRATION OF SOILS LIMED WITH AMOUNTS CORRESPONDING TO THEIR CONTENTS OF EXCHANGEABLE HYDROGEN

It is well established that soil acidity is due to the presence of hydrogen in the exchangeable form. It would seem, then, that the exchangeable hydrogen determination of soils should give an accurate quantitative method for determining the amount of lime that must be added to a soil to bring it to pH 7.0. It seemed desirable, therefore, to lime soils in accordance with their content of exchangeable hydrogen and to determine their reaction after equilibrium between the soil and lime was established. A good opportunity for this kind of study was offered in connection with the work on the first part of this investigation and some other investigations in progress. Some of the results of this study are presented in table 4.

The exchangeable hydrogen was determined by the barium acetate method of Parker (11). Precipitated calcium carbonate was added to the soils in 2-gallon pots in the greenhouse in amounts equivalent to their content of exchangeable hydrogen. The pots were kept watered by the addition of rain water from time to time in amounts necessary to bring the soils to optimum moisture content. After 2, 4, and 6 months the soils were allowed to dry, were mixed thoroughly, and samples were taken for pH determinations. The pH determinations were made by the "dialysis-colorimetric" method (13).

In columns 6, 7, and 8 of table 4 are given the reaction of the soils after 2, 4, and 6 months. It will be noticed that equilibrium is established after a period of about four months. The pH values after 6 months are as a whole slightly higher than those after 4 months, probably because the pots had all been leached with 10 liters of rainwater just previous to their sampling for the 6 months period. As was shown by Crowthers (3), leaching a soil results in slightly increasing its pH value. Since this amount of leaching is greater than ordinarily takes place in the field it is probably better to use the results after 4 months

as expressing the pH values of soils limed in accordance with their content of exchangeable hydrogen. It will be noted that the resulting pH value varied from 6.25 to 6.83 and that most of the ten soils gave very close to the average figure, pH 6.60. When one considers that the original pH of the soils varied from 4.50 to 6.48, the final pH figures were remarkably uniform. It will be noticed that soil no. 671, which had an original reaction of pH 4.50, had the lowest pH value after liming, whereas no. 673, with the highest pH value to start with, had the highest pH value after liming. This would be expected if the same percentage of total acids is neutralized for all soils. It would seem, however, as if the differences would be even greater than is here indicated.

In connection with the work done for the first part of this investigation it was possible to calculate the pH of nine other soils if limed according to their content of exchangeable hydrogen. These results are given in the last column of table 3. It will be noticed that the variation with these nine soils is between pH 6.20 and 6.75, and that the average for all is pH 6.49.

These nineteen soils represent soils of widely different pH value, exchangeable hydrogen content, and texture. In view of these facts the pH values after liming are considered very uniform. This method, then, offers a means of determining the amount of lime that must be added to a soil to bring its reaction to about pH 6.5. It is possible that a much longer period of contact would lower this pH value slightly, for some other investigations now in progress would seem to indicate that although the action is very slow there seems to be a slight decrease in pH value of limed soils even after 6 months contact. This probability might also increase slightly the liming factor given in the first part of this paper. Unlike the buffer method, however, the exchangeable hydrogen method gives no measure of the amounts of lime it takes to bring soils to pH values other than 6.5, as for example; 6.0, or 7.0.

From a theoretical viewpoint the question may well be asked as to why liming in accordance with the exchangeable hydrogen content does not bring soils to pH 7.0. No doubt this is because some of the lime reacts with material other than the exchangeable hydrogen. This point will be elaborated on in the following general discussion.

GENERAL DISCUSSION

The term "lime requirement" of soils has generally been understood to mean the amount of lime necessary to neutralize the total acidity of the soil. Various methods have been used for determining the so-called "lime requirement" of soils. Since, upon comparing these methods, it was found that they often gave widely different values, the term has now a very vague meaning. Several investigators have called attention to this fact. If one uses the term, it must be stated as "lime requirement" by this or that method. Truog (15) believes that the term "lime requirement" should be used in connection with plants rather than with soils, for a soil may not need lime for the growing of some crops while it may need large amounts of lime if other plants are to be grown

on it. It would seem, however, that if the term "lime requirement of a soil" can be used to express something definite with regard to its acidity, it should be retained.

A neutral soil has a pH value of 7.00. The true lime requirement of a soil, then, should be understood to mean the amount of lime it takes to bring it to pH 7.0; and any method that will give this amount should be considered to give the "lime requirement" of that soil. Since it is rarely advisable to lime a soil to pH 7.0 for most farm crops, the term as just defined would have only a limited application. It seems, however, that if we can speak of the "lime requirement of a soil to pH 7.0," we should also be able to speak of the amount of lime it takes to bring a soil to pH 6.0 as the "lime requirement to pH 6.0." Similarly, the lime requirement to any other pH value would also denote something definite about the acidity of soils. This is believed to be the only true sense in which we can speak of the lime requirement of soils. While it is recognized that the optimum pH value for various crops on the same soil, or for the same crop on different soils may vary considerably, it would appear much more significant to speak of the lime requirement of a soil to pH 6.0, 6.5 or 7.0 than to speak of the lime requirement according to this or that method.

The methods presented in this investigation make possible the use of the term "lime requirement" in this more definite sense. By means of the buffer method it is possible to determine how much lime it takes to bring a soil to any definite pH value. It was found that although the amount of base necessary to bring a soil to a definite pH value as determined by the buffer method in the laboratory is smaller than the amount of lime it takes in the field or greenhouse to bring the soil to this pH value, yet the relation between these two values or the "liming factor" is very uniform for soils of widely different characteristics. The "liming factors" for about 80 soils studied in this investigation averaged about 1.50. In other words, it took about one and one-half times as much lime to bring the soil to pH 6.0 or 6.5 when limed in pots with calcium carbonate, as it did $\text{Ba}(\text{OH})_2$ in equivalent amounts according to the buffer method in the laboratory.

The reason for the presence of a "liming factor" is not at once clear unless we assume that three days is too short a time for equilibrium to become established between the soil suspension and base as determined in the laboratory method. If so, what makes the reaction so slow? This point will be discussed more fully when the exchangeable hydrogen data are discussed.

Christensen and Jensen, working with eight Danish soils, obtained a "liming factor" of about 3.0. The most important reason for the difference between their factor and that secured by the writers is probably the fact that they worked with field soils and assumed that the lime they added was confined to the first 20 cm. of surface. They called attention to this point in the discussion of their results. That the downward movement of lime may be considerable has been shown very strikingly by Crowthers (5). In applying the factor of 1.50 to field soils, then, it is important to recognize the probability

of leaching of the lime below the zone for which the value has been calculated. It is evident that the character of not only the surface soil but also that of the subsoil with regard to texture must be considered. Not only that, but the amount of rainfall and the time elapsing after the addition of the lime will affect the amount of downward movement. In applying this factor to field soils it is also important to know the purity of the limestone added and its reactivity. Coarse ground limestone will, of course, react much more slowly than finely ground material. Some of these factors are being further studied by the writers. It is evident, however, that it is only by studying one factor at a time that the true "liming factor" can be established.

The chief advantage of the buffer method of studying soil acidity is that it gives both the quantity and the intensity factor of soil acidity. In most soil acidity methods only one of these factors is considered. If only the quantity factor is considered a very inadequate understanding is given of the acidity of the soil. Thus, for example; one might have two soils, one with a total exchange capacity of 20 and the other 3 mgm. equiv. per 100 gm. of soil. The latter would be representative of quite a few of our sandy soils, while the former would represent an average clay loam soil. Let it be assumed that the amounts of acid present in both soils is the same according to some total acidity method and that the quantity is equal to 2 mgm. equiv. of hydrogen. In case of the sandy soil two-thirds of the exchange complex would be saturated with hydrogen, while in case of the clay soil only one-tenth of the complex would be tied up with the hydrogen. These two soils would be expected to respond quite differently to lime, and yet the total acidity methods would give no indication of this. The pH determination on these two soils, however, would indicate the difference in their percentage saturation. The pH of the sandy soil would probably be about 4.8, whereas that of the clay soil would probably be about 6.5. Such cases have actually been encountered. Thus, whereas the clay soil would undoubtedly not require lime the sandy soil would be benefited by liming. The buffer method would also make possible a fairly accurate determination of the amount of lime it takes to bring this soil to pH 6.5 and would insure against the possibility of overliming, which might be detrimental. On the other hand, whereas pH determinations alone may give a fairly accurate idea of whether a soil needs lime, they give no indication of how much lime is needed. Since the buffer method includes not only a determination of the pH value of the soil, but also a determination of the amount of lime required to bring that soil to any definite pH value, its advantages are self-evident.

What has been said with regard to applying the buffer method to the determination of the amount of lime required to bring the pH of field soils to definite reactions will also apply to the exchangeable hydrogen method discussed.

The exchangeable hydrogen method makes possible the determination of the amount of lime required to bring soils to pH values of about 6.5, and in

combination with pH determinations it should prove of considerable value in making definite liming recommendations.

Liming in accordance with the content of exchangeable hydrogen, however, did not bring the soils to pH 7.0 as might have been expected. In accounting for this apparent discrepancy, two explanations seem possible: Either the lime added reacts with other material than exchangeable complex, or the method for exchangeable hydrogen does not determine the total amount of acids in the soil, the dissociation of which is such as to give a pH value of less than 7.0. Parker (11) has shown, however, that the soils after being leached with barium acetate, in the determination of exchangeable hydrogen, have a pH of very near 7.0. It would seem, then, as if the first of these reasons may give the true explanation. That the calcium carbonate reacts with other material than the exchangeable hydrogen is substantiated by experiments conducted by the writers and which are soon to be published. It was found in that study that only a part of the calcium added to soils as calcium carbonate replaced H in the exchangeable form. This indicates that the soil contains material, apparently in a non-exchangeable form, which will react with the calcium of calcium carbonate. Thus, when lime is applied in amounts necessary to neutralize the exchangeable hydrogen, and only a part of the lime added is used for this purpose, it is evident that the soil will still contain some exchangeable hydrogen and that the resulting reaction of the soil will be below pH 7.0.

This fact will also explain the presence of a "liming factor." In the buffer method of determining the amount of base required to bring a soil to a definite pH value, the base reacts nearly entirely with the exchangeable hydrogen. On the other hand, when lime is added to a soil and a long time of contact is allowed, the lime reacts not only with the readily reactive exchangeable hydrogen but also with other material of a non-exchangeable character. A further study of this interesting point is being conducted. It promises to throw some light on the relation between the exchangeable and non-exchangeable soil complex.

SUMMARY

The experiments reported in this paper were undertaken with the following purposes: 1. To work out a simple method for the determination of the buffer action of soils toward base; 2. To determine the correlation between the buffer action of soils toward base as determined in the laboratory and the amounts of lime required to bring soils to definite pH values by liming; 3. To determine the H-ion concentration of soils limed in accordance with their content of exchangeable hydrogen. The results of the experiments may be briefly summarized as follows:

1. The buffer capacity of soils toward base can be determined in the laboratory by means of the "dialysis-colorimetric" method. A 3-day period of contact between the soil and Ba(OH)₂ was found to be sufficient for the establishment of equilibrium.
2. The H-ion concentration of soils after being treated with base in the laboratory, according to the buffer method, was lower than that of the soils treated with equivalent

amounts of lime in greenhouse pots. The relation between the amounts of base required in the laboratory and the amounts of lime required in field or greenhouse to bring soils to similar pH values is called the "liming factor."

3. The "liming factor" of 77 soils of widely different texture and acidity was found to be noticeably uniform and to average about 1.50.

4. Liming of soils in accordance with their content of exchangeable hydrogen brought the soils to pH values of about 6.5.

5. The determination of the buffer action of soils toward base and the determination of the exchangeable hydrogen of soils are recommended as methods of determining the amounts of lime required to bring soils to definite pH values. The advantages of these methods are briefly discussed.

6. The reason why soils to which have been added amounts of lime equivalent to their content of exchangeable hydrogen, do not reach a pH of 7.0 but only of about 6.5, is believed to be because the lime reacts with other than the exchangeable hydrogen of soils.

7. The non-exchangeable soil complex is also believed to be responsible for the presence of the "liming factor."

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THE INFLUENCE OF FERTILIZER TREATMENTS ON THE CONTENT OF EXCHANGEABLE CATIONS IN HAGERSTOWN SILT LOAM¹

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The relative amount and proportion of cations in the so-called replaceable condition give promise of being some of the most important characteristics of soils. Cation exchange studies carried on by Gedroiz (6, 7, 8, 9, 11, 12, 13), deSigmund (26), Hissink (14, 15, 16), Kappen (20), Weigner, (28), Kelley (21, 22), Page (25), and many others have given us a clearer understanding of the phenomena involved in soil acidity, soil alkalinity, absorption, physical properties, hardpan formation, availability of plant nutrients, secondary effect of fertilizers, and amendments. Even the mechanism by which nutrient ions may leave the soil to enter the plant is made clearer. A measurement of the content of exchangeable cations affords one of the best tools with which to study the variations in the different soil horizons. The literature on the subject has been so well reviewed recently that it is unnecessary to consider it here. The findings of the workers mentioned are in close agreement with one another. The present methods for determining absorbed or exchangeable cations may be arranged into three groups as follows:

1. *Treatment with neutral salt solutions.* Some of the salts used by different investigators are NH_4Cl , NaCl , KCl , CaCl_2 , BaCl_2 , and $(\text{NH}_4)_2\text{C}_2\text{H}_5\text{O}_2$. Usually normal or half normal strength is used, although stronger or more dilute solutions may be used, thereby shortening or lengthening the period of extraction. Extraction is usually effected by treating 10, 25, or 50 gm. of soil with an excess of the salt solution by continued percolation. By mass action the cation of the salt finally replaces all, or nearly all, of the cations held in the absorbed condition. The choice of the salt used depends upon whether or not it interferes with subsequent chemical analyses of the percolates. Ammonium chloride has met with most favor because it may be removed by volatilization. The ammonium ion is believed to be present in negligible quantities in soil. Barium chloride, which has been used for some time in determining exchangeable hydrogen, has been recommended by Burgess and Brezeale (2), for other cations as well. The barium ion is not to be found in the soil complex, hence the barium salt causes no serious analytical difficulty.

2. *Treatment with dilute acids.* Normal and tenth normal HCl , HNO_3 , H_2CO_3 , and $\text{HC}_2\text{H}_5\text{O}_2$ have been used. When acids are employed, the H ion replaces all, or nearly all, of the absorbed cations and is especially effective because it has a high energy of absorption and hence a high replacement value. Gedroiz (10), having used NH_4Cl for many years,

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concludes that 0.05 *N* HCl may serve the purpose quite as well. Kelley (22) obtained practically the same quantities of the respective elements Ca, Mg, K, and Na with 0.04 *N* HCl as with *N* NH₄Cl. Analytical procedures are simplified when acids are used, although more Fe, Al, and Mn may be brought into solution than with salts. It is also true that acids have a high solvent power on calcium carbonate, calcium sulfate, and other salts as well as on some unaltered minerals. There is, however, little fundamental difference between the action of acids and neutral salts as means of extracting exchangeable cations.

3. *Removal by electrodialysis.* The principle of the electrical endosmose was employed by Ormondy in the purification of clay. More recently Mattson (23), Bradfield (1), and others have employed it to determine the exchangeable cations, and anions as well, insofar as the latter are diffusible through membranes. Although there are numerous variations in the types of dialyzers and in the choice of electrodes (17, 18), the principle is as follows: The soil is separated from the anode and cathode chambers of a dialyzer by a parchment or similar membrane. The slight dissociation of the absorption soil complexes yield small quantities of cations and anions. These migrate through the respective membranes and are collected in the cathode and anode chambers. Dissociation and dialysis continue until all of the exchangeable ions have been removed. The results obtained by electrodialysis are in agreement with those obtained by neutral salt extraction.

It is evident that many, if not all, commercial fertilizers must exert a certain degree of ion replacement. The effect would be scarcely noticeable except by the continuous use of salts with the same cation in rather large amounts. This secondary or residual effect of fertilizers has been noted in many instances. Thus we have the puddling action of nitrate of soda due to the peptizing action of the Na ion in the so-called zeolitic complex. Less marked results have been observed when potassium salts are used; probably because they are used in smaller amounts, and the K ion is utilized by plants. Ammonium salts have produced the most spectacular residual effects due to the H ion from the H₂SO₄ and HNO₃ which must follow the use of this salt. Even organic fertilizers and farm manure, because of the carbonic, nitric, and other acids, should cause a successive replacing of the H ion for the other cations of the complex.

The effects of the long-continued use of fertilizers on the Broadbalk wheat plots of Rothamstead were studied by Page (24). The results he obtained were not so marked as might have been expected, no doubt because of the high content of calcium carbonate in the soil. It will be remembered that these plots were heavily chalked before the experiment was begun. This high content of highly reactive calcium has protected the so-called exchangeable calcium from being replaced even by ammonium salts. Burgess and Pember (3), have shown that fertilizer treatments materially alter the amount of exchangeable calcium; that is, the calcium replaceable with carbonic acid. Joffe and McLean (19) have shown that treatments with ammonium sulfate have reduced the quantity of replaceable Ca ions and in their place have substituted H ions.

EXPERIMENTAL

It would seem that the general fertilizer experiment at the Pennsylvania Experiment Station might give some of the most useful evidence that could be obtained concerning the fundamental effects of fertilizer treatments upon the

soil proper. It has been under continuous treatment for 46 years, and the treatments and yields have been published periodically in station bulletins

TABLE 1
Chemical analysis of Hagerstown silt loam

	SURFACE 9.5 IN.	SUBSURFACE 9.5-18.5 IN.	SUBSOIL 18.5
	per cent	per cent	per cent
SiO ₂	72.320	67.720	63.230
Al ₂ O ₃	10.192	13.503	15.994
Fe ₂ O ₃	3.710	5.580	6.840
FeO.....	0.540	0.350	0.207
V ₂ O.....	0.036	0.090
Cr ₂ O ₃	0.002	0.002
TiO ₂	0.340	0.480	0.440
P ₂ O ₅	0.102	0.102	0.077
ZrO ₂	0.037	0.045	0.050
MnO.....	0.240	0.250	0.230
CaO.....	0.660	0.650	0.900
MgO.....	0.650	0.980	1.370
BaO.....	0.009	0.019	0.019
SrO.....	0.016	0.022	0.033
K ₂ O.....	3.960	4.220	4.420
Na ₂ O.....	2.280	1.280	1.350
S.....	0.062	0.051	0.062
SO ₃	0.017	0.020	0.017
Loss on ignition.....	5.300	5.000	5.500

TABLE 2
Fertilizer treatment on corn and wheat in rotation

PLOT NUMBER	TREATMENT	POUNDS PER ACRE		
		N	P ₂ O ₅	K ₂ O
2	Dried blood	24		
3	Dissolved bone black (acid phosphate)		48	
4	Muriate of potash			100
16	Manure—6 tons	59	38	52
21	Blood, acid phosphate, muriate of potash	72	48	100
23	Burned lime (2 tons on corn)			
25	Acid phosphate, muriate of potash		48	100
28	NaNO ₃ , acid phosphate, KCl	72	48	100
32	(NH ₄) ₂ SO ₄ , acid phosphate, KCl	72	48	100
36	Nothing			

(5). The rotation consists of (a) corn, (b) oats, (c) wheat (d) timothy and clover. The fertilizers are applied to the corn and wheat.

The soil was formed by the residual weathering of limestone. The calcium

carbonate has been practically completely leached from the surface soil and upper horizon of the subsoil. Only the horizon close to the rock contains any appreciable carbonate. There are occasional spots throughout the soil series, and even on the fertilizer plots, where the limestone is so close to the surface that the dissolving carbonate saturates the complex, and in these spots the soil is neutral. Everywhere else the soil is acid in its natural state. The chemical and mineralogical analysis of virgin soil of this series as given by Thomas (27) is shown in table 1.

For this experiment certain plots on tier I were chosen. This tier was in clover at the time of sampling, hence no fertilizer was applied that year. Samples were drawn on July 1. Each represents a composite of eight borings taken 6 inches deep. The plots shown in table 2 were chosen for study.

METHODS

Fifty-gram portions of the moist soil were thoroughly shaken with 250 ml. of 0.1 *N* HCl and thrown on the filter. The residue was washed with repeated additions of 0.1 *N* HCl until the leaching gave no test for calcium. The filtrate was made up to definite volume. No attempt was made to distinguish between the dissolved and displaced cations. In the opinion of the writer the calcium in calcium carbonate, for example, is as available as and probably more available than that held in the silicate complex.

A 200-ml. aliquot was analyzed for exchangeable ammonium. The remainder was evaporated, the silica dehydrated, and the solution analyzed for Al, Fe, Ca, Mg, K, and Na. All determinations were made by standard gravimetric methods and the results represent closely agreeing duplicates.

The exchangeable hydrogen was determined as suggested by Gedroiz (11) with slight modifications. Ten-gram portions of soil were placed in centrifuge tubes with 100 ml. of normal BaCl₂ and thoroughly puddled with a glass rod. The suspension was centrifuged and the supernatant liquid filtered. This operation was repeated until the leachings were found to have nearly the same hydrogen-ion concentration as the original BaCl₂ solution. A large quantity of solution was required to accomplish this. The entire filtrate was titrated with 0.02 *N* KOH using brom cresol purple as indicator. The results, calculated on the dry soil basis, are presented in table 3. When the BaCl₂ extracts were titrated it was noticed that the ones having the greatest amount of replaceable hydrogen gave a precipitate of hydroxides of Al and Fe at about pH 5.5.

In interpreting the results, it should be noted that at the end of tier I, where plots 2, 3, and 4 are located, the limestone is close to the surface, and the dissolving carbonate has saturated the complex with calcium. The soil is neutral. Hence the data given for these three plots do not represent the effects of the fertilizer treatment, but rather the influence of the limestone, at least as far as exchangeable Ca is concerned.

DISCUSSION

The data given in table 3 as percentages have been expressed in milligram equivalents in table 4 and the relative proportion of each is given in table 5.

Aluminum and iron. Fertilizer treatments appear to have made no significant difference in the quantity of these elements soluble in 0.1 N HCl. The soil has not reached that degree of unsaturation at which added substances displace trivalent cations.

TABLE 3
Cations removed with 0.1 N HCl. Per cent of dry soil

PLOT	TREATMENT	Al	Fe	Ca	Mg	K	Na	NH ₄	H	pH
2	Blood	0.053	0.016	0.188	0.024	Lost	Lost	0.0048	0	7.12
3	Acid phosphate	0.160	0.016	0.189	0.010	0.0089	0.0098	0.0034	0	7.00
4	KCl	0.208	0.016	0.267	0.022	0.0232	0.015	0.0014	0	7.32
16	Manure	0.149	0.016	0.102	0.007	0.0052	0.012	0.0041	0	5.67
21	Blood, P, K	0.188	0.024	0.064	0.005	0.0127	0.012	0.0041	0.00073	5.00
23	CaO	0.148	0.015	1.293	0.008	0.0047	0.025	0.0057	0	8.27
25	P, K	0.168	0.013	0.077	0.006	0.0130	0.011	0.0049	0.0013	5.50
28	NaNO ₃ , P, K	0.138	0.015	0.077	0.003	0.0152	0.011	0.0028	0.00088	5.33
32	(NH ₄) ₂ SO ₄ , P, K	0.172	0.016	0.016	0.0004	0.0158	0.012	0.1143	0.0041	4.15
36	Nothing	0.124	0.013	0.105	0.007	0.0042	0.012	0.0028	0.00021	6.27

TABLE 4
Milligram equivalents of exchangeable cations in 100 gm. of dry soil

PLOT	Al	Fe	Ca	Mg	K	Na	NH ₄	H
2	5.7	0.87	9.4	2.04	Lost	Lost	0.28	0
3	17.7	0.87	9.4	0.84	0.23	0.42	0.20	0
4	23.1	0.87	13.4	1.82	0.60	0.65	0.08	0
16	16.5	0.87	5.0	0.62	0.13	0.52	0.24	0.73
21	20.7	1.29	3.0	0.40	0.32	0.52	0.22	2.33
23	16.5	0.81	64.6	0.66	0.12	1.08	0.32	0
25	18.6	0.69	3.8	0.50	0.33	0.47	0.28	1.3
28	15.3	0.78	3.8	0.24	0.39	0.50	0.16	0.88
32	19.2	0.87	0.8	0.34	0.40	0.54	6.72	4.1
36	12.9	0.69	5.2	0.58	0.11	0.52	0.16	0.2

Calcium. The comparatively large quantity of exchangeable Ca in plots 2, 3, and 4 has already been explained by the closeness of the limestone to the surface. (It must not be inferred from these data that blood or muriate of potash does not hasten the loss of replaceable Ca.) The manured plot contains about the same quantity as the unfertilized plot. The continued use of burned lime on plot 23 has built up a large reserve of this element in the complex. Plot 32, receiving ammonium sulfate with phosphorus and potash, and plot 21, receiving dried blood with phosphorus and potash, are by far the most acid plots particularly the former. In both these plots the exchangeable Ca is

reduced to a very low figure. A comparison of plot 28 with plot 32 shows nearly five times as much replaceable calcium in the nitrate of soda plot as in the one receiving ammonium sulfate. It is not possible from these data to determine the effect of acid phosphate on exchangeable calcium.

Magnesium. The magnesium content of plots 2, 3, and 4 is high for the same reason that the calcium content is high. The limestone underlying the soil is dolomitic. The three plots receiving the heaviest applications of complete fertilizer; namely, plots 21, 28, and 32, contain the least exchangeable Mg. As might be expected, liming has protected the magnesium against loss.

Potassium. In every case those plots which have received potash fertilizers contain a significantly larger quantity of this element than do the remaining plots. It appears that a part of the potassium, applied as soluble salts, is fixed in the exchangeable form. This confirms the observations of Frear and Erb (4) drawn from work on tier II of the same field experiment.

TABLE 5

Relative proportion of cations expressed in per cent of total divalent and monovalent cations

PLOT	Ca	Mg	K	Na	NH ₄	H
2	80.2	17.4	Lost	Lost	2.4	0
3	84.7	7.5	2.2	3.8	1.8	0
4	81.0	11.0	3.7	3.9	0.4	0
16	69.1	8.5	1.8	7.2	3.3	10.1
21	43.6	5.8	4.7	7.6	3.2	33.9
23	96.7	1.0	0.2	1.6	0.5	0
25	56.9	7.5	4.9	7.0	4.2	19.5
28	63.6	4.0	6.5	8.4	2.7	14.8
32	6.2	2.6	3.1	4.2	52.1	31.8
36	76.8	8.6	1.6	7.7	2.4	2.9

Sodium. The only significant difference found in the quantity of exchangeable sodium is in plots receiving nitrate of soda (table 5). The possibility of analytical error in the sodium determination is great.

Ammonium. Most investigators have considered the quantity of exchangeable ammonium to be insignificant. A glance at these figures shows it to be small in most cases. The sulfate of ammonium plot, no. 32, contains more absorbed NH₄ than any other ion. It is quite evident that the ammonium ion has been displacing large quantities of the Ca ion. In fact, it has nearly exhausted it. As shown in table 3, 52 per cent of the absorbed divalent and monovalent cations consist of NH₄ ions.

Hydrogen. Plots 2, 3, and 4, being saturated with Ca, contain no replaceable H. Continued liming of plot 23 has also saturated the absorption complex. The effects of sulfate of ammonium and of dried blood are clearly shown to exhaust the calcium and replace it with H. Manure and mineral fertilizers tend to produce the same results, only less marked.

The considerations just discussed are more clearly shown in table 4, giving the milligram equivalents of each ion found in 100 gm. of dry soil.

In table 5 is given the relative proportion in milligram equivalents of the divalent and monovalent cations expressed as a percentage of the total divalent and monovalent equivalents. This table shows very clearly what has been going on in the soil as a result of the long-continued fertilizing. The two plots in which the replaceable calcium is becoming exhausted are so acid that crops grow poorly. The sulfate of ammonium plot in particular produces very poor crops of corn, oats, and wheat, and when timothy and clover are sown nothing but sorrel and redtop grow.

SUMMARY

Under the conditions of this experiment the following conclusions seem possible:

1. When soil is repeatedly fertilized with commercial fertilizers or with organic manures, significant changes take place in the quantity and proportion of the so-called replaceable cations.
2. Liming tends to saturate the absorption complex with calcium.
3. A part of the potassium applied in commercial fertilizers is retained in the acidoid complex.
4. Under suitable conditions, the NH_4 from ammonium salts may be retained and constitute a large percentage of the total absorbed cations.
5. Sulfate of ammonium in the amounts used in this experiment has nearly exhausted the active calcium and replaced it with NH_4 and H ions.
6. Other fertilizer salts tend, in a lesser measure, to exhaust the readily attackable calcium, replacing it with H ions.

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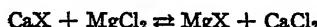
THE IDENTIFICATION AND COMPOSITION OF THE SOIL ALUMINO-SILICATE ACTIVE IN BASE EXCHANGE AND SOIL ACIDITY¹

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In a previous article (4), the writer reported the results of an investigation on the nature of the base exchange reaction of soils and zeolites. The zeolites are a class of hydrated alumino-silicates of the general formula—(R₂O or RO)(Al₂O₃·x SiO₂·y H₂O)—or, more simply, for the calcium compounds, CaX, where X is the dibasic alumino silicic acid radical. The reaction for such a compound with a solution of MgCl₂ may be written:



It was found that the equilibrium point was governed by both the concentration of the magnesium chloride solution and the amount of zeolite employed. In applying the law of mass action to the equilibrium conditions, then, it is necessary to consider the active masses of the four reactants. As an approximation, the active masses of the bases in the solid phase were regarded as proportional to their total concentrations; and the ionic concentrations of Ca and Mg were taken for the liquid phase. This gives then, at equilibrium:

$$K = \frac{(\text{Mg}^{++})(\text{CaX})}{(\text{Ca}^{++})(\text{MgX})} \quad (4)$$

The values for K obtained with a series of zeolites and soils fulfilled these conditions, within the limits of experimental accuracy.

Recently, a more carefully planned experiment was carried out, with greater precision, in order to test more rigorously the degree of reliability of the theory. The material used was a slightly acid subsoil taken at a depth of 3 feet, from a Hawaiian sugar cane field. The exchange complex in a lot of this soil was

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saturated with Ca by the method³ of continuous leaching with CaCl_2 solution; the residue was washed free from chloride with water. Eight 25-gm. samples of the treated soil were then transferred to shaking bottles and treated with equal volumes of solutions of MgCl_2 , the concentrations of which ranged from 0.006–0.013 N. The equilibrium concentrations of Ca and Mg in the extracts were determined after adequate shaking of the suspensions. The total exchangeable Ca was estimated in the leachings obtained by the usual method of continuous extraction of a separate sample with a normal solution of NH_4Cl . The values obtained are given in table 1. The mean value for K is 1.415 \pm .009—a result, the accuracy of which is well within the limits of experimental error.

IDENTIFICATION OF THE ALUMINO-SILICATE ACTIVE IN BASE EXCHANGE

The similarity between the exchange reaction processes for zeolites and soils, strongly suggests that compounds of a zeolitic nature are responsible for this important soil phenomenon. It has long been known that if a sample of soil be boiled with 20 per cent HCl, the base exchange property is destroyed, and this is accompanied by the extraction of Al_2O_3 and SiO_2 . It has been shown, also, that the soil humates play an active part in the exchange process, and if one wishes to study the inorganic portion of the exchange complex, it is necessary to remove the organic matter. It has been found that a 6 per cent solution of hydrogen peroxide is useful in this respect, and its action does not impair the properties of the alumino-silicates. This method was employed in the preparation of a large sample of Colby silt loam which was used in this investigation.

Two main lines of attack for identifying the active alumino-silicate readily suggest themselves: 1. To isolate the alumino-silicate itself by mechanical means; 2. To decompose the compound with an acid of suitable concentration and to determine the proportions of Al_2O_3 and SiO_2 liberated by the process. Both methods were tested in a preliminary study.

Mechanical separation of active alumino-silicate

If it is possible to obtain even a small quantity of the mineral in the crystalline condition the particles of which are not less than 0.005 mm. in diameter, the method of optical identification might readily be employed. Now many workers have determined the distribution of the base exchange capacity among the various soil fractions obtained by mechanical analysis. Gedroiz (2) gives a summary of their findings. It has been observed that the clay fraction contains the bulk of these active alumino-silicates, but that even the silts and fine sands possess the property to an appreciable degree. The question arises: Are the particles which confer this property crystalline individuals of the sizes indicated, or are they present as colloidal coatings which have not been completely removed from the larger particles during the process of dispersion of the

*This method will be referred to as "method 1."

sample? Anderson and others (1) have shown the difficulty involved in the removal of the colloidal material from the silt and sand. Prolonged mechanical attrition was necessary in order to effect a separation.

An attempt was made to test this question with the silt separated from the Colby silt loam. The preliminary treatment of the sample with hydrogen peroxide resulted in a high degree of dispersion of the soil, and this was further assisted by a subsequent shaking of the suspension for 48 hours. A few drops of ammonia were added to the water. The silt fraction was separated by the centrifugal method, and, when examined microscopically, the particles appeared to be free from colloidal aggregates. The individual grains also possessed fairly clean surfaces, although many showed pitted areas. The base exchange capacity of this sample was found to be 4.7 milliequivalents per 100 gm. To determine whether the colloids had been completely removed, the sample was again shaken in water, with the addition of a number of steel balls (4 mm. diameter) to aid in the disruption of the aggregates; these balls did not break up the individual grains to any extent. Twenty-four hours of this treatment gave considerable turbidity to the suspension. The clay was separated as before, and the base exchange capacity of the residual silt was determined. Repetition of the treatment gave a further small amount of clay, but the removal appeared to be almost complete. The results of these separations are as follows:

TREATMENT	CLAY REMOVAL PER 100 GM. SILT	BASE EXCHANGE CAPACITY PER 100 GM.	
		gm.	milliequivs.
None.....	4.7
First treatment.....	2.5	2.5	3.7
Second treatment.....	0.8	0.8	3.4

The residual silt, thus, still possessed appreciable base exchange capacity.

By the use of Thoulet's solution, an attempt was made to concentrate the base exchange material in the silt. The zeolites as a class have characteristic ally low specific gravities, and their separation by this method should be achieved readily. By regulating the specific gravity of the liquid, it was possible to separate the sample into 4 convenient fractions. The base exchange capacity of each fraction was determined, and the following results were obtained:

SPECIFIC GRAVITY OF FRACTION	WEIGHT OF FRACTION	BASE EXCHANGE CAPACITY PER 100 GM.
	gm.	milliequivs.
2.67<	19	3.78
2.63-2.67	67	1.69
2.61-2.63	32	3.93
<2.61	21	4.17

It is seen that no appreciable segregation of the exchange material was effected. Now there was good evidence, from other tests, to indicate that the active mineral in this soil sample was all of one kind, and thus should be separable in one and only one fraction. The obvious conclusion was that the colloidal material had not been completely removed from the silt grains, and this fine material was responsible for the base exchange activity.

It is interesting to note, from these results, that the largest fraction (specific gravity 2.63-2.67) possessed the poorest exchange capacity. This fraction contained the quartz particles of the silt. One would expect that the surfaces of these particles, from their nature, would permit less firm adherence of colloid than the weathered and pitted surfaces of a mica or a feldspar particle.

The separates were mixed once more, and rubbed in a mortar very gently with a rubber tipped pestle; a little water was added to make a thin paste. By this method, very large amounts of colloid were again separated, and periodic tests showed a gradual diminution in the base exchange capacity of the residue. After continuing this tedious process for some hours, the residual silt was freed from practically all of its colloid, and concurrently the base exchange capacity disappeared.

It must be concluded, then, that the base exchange capacity of the soil resides entirely in the colloidal—or, at least, in the clay—fraction. The results also confirm the findings of the workers of the Bureau of Soils regarding the difficulty of removing completely the colloidal material from the larger soil particles. In the experiment just described, colloidal material equal to 12 per cent of the sample was removed from the silt particles, which had been more carefully freed from clay than is demanded by the Bureau of Soils' method for mechanical analysis.

Chemical separation of active alumino-silicate

The zeolites, particularly when in the colloidal state, are very unstable toward even dilute solutions of HCl, and it was thought that their existence in the soil might readily be demonstrated by treating a sample with an appropriate solution of this acid. The soil is a heterogeneous mixture of unweathered rock and mineral particles and various products of chemical decomposition; of the latter we know little concerning the individual minerals which compose it. It contains, undoubtedly, some free colloidal silicic acid, as well as Fe_2O_3 and Al_2O_3 in a more or less hydrated condition. Any method which depends on the solvent action of an acid for its extraction of zeolitic alumina will yield results of low reliability if steps are not taken to remove, first of all, the soluble free Al_2O_3 from the sample. A similar complication arises also in the subsequent removal of silicic acid liberated in the decomposition of the zeolite.

Van Bemmelen (5) first proposed the use of HCl, specific gravity 1.19, for the decomposition of the zeolitic minerals of the soil, but Gedroiz has shown

that acid of this concentration decomposes, in addition, soil minerals which are not zeolitic. Consequently, an acid of considerably lower concentration was tried in these experiments. Gedroiz used the method of extraction with 0.05 *N* HCl to remove the exchangeable bases and reported but little decomposition of the exchange complex by its action. On the basis of these findings, the following method was developed.

A 10-gm. sample of Colby silt loam (which had been treated repeatedly with H_2O_2 to remove organic matter) was leached with about 2 liters of 0.05 *N* HCl, to remove the soluble free Al_2O_3 and Fe_2O_3 . The colloidal silicic acid was extracted from the residue by boiling for 15 minutes with 150 cc. of 10 per cent Na_2CO_3 solution, to which had been added a few drops of NaOH solution. The extract was decanted and the process repeated. The residue was finally washed with 2 per cent Na_2CO_3 solution. A determination of the base exchange capacity of the residue showed that the zeolitic compounds had not been affected by the treatment. The sample was then transferred to a 500 cc. flask and boiled under reflux for 6 hours with 200 cc. of 0.2 *N* HCl. The extract was analyzed for SiO_2 , Fe_2O_3 , and Al_2O_3 . The residue, after being washed free from acid, was extracted twice with 150 cc. of 10 per cent Na_2CO_3 as before, and the silicic acid in the extract determined.

It was found that this treatment completely decomposed a sample of colloidal zeolite which had been tested.

The results of the extraction of the Colby silt loam are as follows:

TREATMENT	AMOUNT DISSOLVED		
	SiO_2	Al_2O_3	Fe_2O_3
	per cent	per cent	per cent
Extraction with 0.05 <i>N</i> HCl.....	0.64	0.16
Extraction with 10 per cent Na_2CO_3 (preliminary).....	0.35	0.64	0.16
Extraction with 0.2 <i>N</i> HCl }.....	2.01	1.09	0.94
Extraction with 10 per cent Na_2CO_3 (final) }			

The base exchange capacity of the original material and residue was also determined; this showed:

	<i>milliequivalents</i> <i>per 100 gms.</i>
Exchange capacity of original material.....	8.4
Exchange capacity of residue.....	3.0

It is seen that this treatment was successful in decomposing somewhat more than one half of the active alumino-silicate, but the results were obscured by the solution of 0.94 per cent of Fe_2O_3 , which, it is felt, existed in the soil as the free oxide; this threw some doubt on the source of the Al_2O_3 extracted by the treatment, for some of this may have been present in the condition of the free oxide which was not removed by the preliminary acid extraction. Altogether, the method was not satisfactory, because of the complicating factors which entered.

The use of the base exchange equilibrium constant as a criterion of mineral identity

In the investigation of the exchange reaction with soils and zeolites, each independent sample or compound was found to possess its characteristic equilibrium constant. Hence, if two samples of mineral give identical equilibrium constants for the exchange reaction between, say, calcium and magnesium, it is evidence of their identity; if they further give identical constants when another pair of bases is employed, it might be safely concluded that the identity of the two minerals is established. This method was applied in an attempt to elucidate the constitution of the active alumino-silicate (or alumino-silicates) in the soil. Three important Wisconsin soil types were chosen, and samples of each were oxidized with 6 per cent H_2O_2 until the organic matter was destroyed. The equilibrium constants for the Ca-Mg exchange were next determined. This was carried out in the manner next described (method 2), which is convenient, rapid, and accurate.

Twenty-five gram samples of the soils were placed in 1-liter flasks, and to each was added 500 cc. of a solution of which the concentration was 0.5 N with respect to both $CaCl_2$ and $MgCl_2$. The suspensions were agitated continuously for 12 hours with a mechanical shaker. The extracts were removed by filtration, and suitable aliquots (2 cc.)⁴ were taken for analysis. The residual soils were leached on a Büchner funnel until free from chlorides. The dried samples were then extracted with a normal solution of NH_4Cl in the usual manner, and the Ca and Mg determined in the extract. It will be seen that the substitution of these corresponding values in equation (A) should give an accurate measure of K .

When the 3 soils selected were treated in this manner, they yielded the following results:

	$K. (Ca/Mg)$	$K. (NH_4/K)$
Colby silt loam.....	1.40	1.04
Knox silt loam.....	1.36	1.01
Miami silt loam.....	1.89	0.91

The close similarity of these results, for the former pair at least, is rather striking. These two soils are of widely different origin. The NH_4/K reaction was also studied, and the results are given in the last column. Again the Colby and Knox are in agreement, while the Miami shows an appreciable divergence.

A number of zeolites, both natural and artificial, were tested by the same method; in every instance the equilibrium constants for the Ca-Mg reaction lay between the values 2.5-7.0; in no case did the value obtained approximate

⁴ Since it is only the relative concentrations of Ca and Mg that are of importance in this connection, and since the determination of both Ca and Mg is made on the same aliquot, it is not necessary to measure the aliquots with extreme accuracy.

those shown by the soils. The only substance which looked at all promising was a sample of a clay-like material—bentonite—which gave a K value of 1.12. This interesting clay substance has recently received considerable attention from mineralogists, and colloid chemists have been interested in the peculiar property shown by certain samples, of giving a highly colloidal dispersion with water. The conditions under which this material is produced in nature resemble closely those which effect soil formation, while many of its properties are suggestive—in an accentuated manner—of the corresponding soil characteristics, such as its property of water imbibition with swelling, and pronounced contraction on drying, high degree of hygroscopicity, etc. Many samples possess these properties only to a limited degree. These properties seem to be closely related to the colloidal structure of individual specimens.

Attempt to show the identity of the base-exchange complex of soils and bentonite

Further attempts were made to establish the identity of the active base exchange complex of soils with that present in bentonite. The discrepancy in the K values of the soils may have been caused by the heterogeneous nature of the active soil material, due to either the presence of active organic acids which were not completely removed by the treatment with H_2O_2 , or to the heterogeneous nature of the active alumino-silicates themselves.

The available evidence negatived the latter possibility; for, after about one half of the active alumino-silicate of the soil had been removed by extracting a sample of Colby clay with 0.2 N HCl, the equilibrium constant shown by the residue varied but slightly from that of the original sample. It is scarcely possible that a mixture of two or more active alumino-silicates would be removed at proportionate rates to maintain a constant equilibrium value.

The first possibility appeared more reasonable. The samples employed previously were taken for the determination of organic carbon by the wet combustion method. The results obtained were:

per cent carbon	
Colby silt loam.....	0.11
Knox silt loam.....	0.08
Miami silt loam.....	0.18

In the results previously reported (3) by the writer, it was shown that the equilibrium value for the Ca-Mg exchange of the organic acids in a sample of peat was approximately 4.5. Hence, the presence of a small percentage of active organic matter in the sample might exert a very appreciable influence on the equilibrium constant of the mixture. The carbon contents found are rather low, to be sure, but humic acids have comparatively low equivalent weights, and undoubtedly the products of oxidation by hydrogen peroxide would be active acids.

Gedroiz (2) has shown that if an attempt be made to remove the organic matter from the soil by ignition, the exchange property of the mineral residue

is also destroyed. However, it was thought that prolonged ignition at a comparatively low temperature might achieve the desired result, and leave the activity of the alumino-silicate largely, if not entirely, unimpaired. The sample used for this purpose was a heavy lowland clay, rich in organic matter, taken from a Hawaiian sugar plantation. Twenty-five-gram samples were placed in porcelain dishes and ignited for 30 hours in an electric furnace. Unfortunately, the facilities for the determination of the exact temperature were not at hand, but the temperature was judged to be between 300 and 400°C. It was certainly very much below "dull red" heat. At the end of the period, the soil was of a bright red color, and all organic matter appeared to have been destroyed. As a further check, one half of the material was reignited at the same temperature for a further period of 18 hours. Both samples were employed in a determination of the equilibrium constant for the Ca-Mg exchange as described in method 2. The results obtained were:

SAMPLE	CONSTANT - K
1. Once ignited.....	1.18
2. Twice ignited.....	1.10

These results afford strong evidence in support of the contention that the active alumino-silicate present in the soil is identical with that found in bentonite. Moreover, it seems very possible that this compound is of widespread occurrence in soils, under wide and varied conditions. Thus, it is found in the Wisconsin glaciated soils and also in those formed under humid tropical conditions, from volcanic lava, in Hawaii.

If this identity be granted, one might confine one's attention to the extraction of the active alumino-silicate from bentonite, which is a decidedly easier task than the elucidation of its nature by employing a very heterogeneous material such as soil. Bentonite is itself a mixture of at least two minerals, and its colloidal nature is a serious barrier to any attempt to separate the constituents by mechanical means.

Larsen and Wherry (4) have carried out a considerable amount of work on the constitution of this clay-like material, and conclude that it is made up, in the main, of a mineral which they call "beidellite." On the basis of their analyses they give it the formula $\text{Al}_2\text{O}_3 \cdot 3 \text{ SiO}_2 \cdot x\text{H}_2\text{O}$. A glance at the analyses of the samples on which they base their conclusions will convince one that the lack of uniformity of the compositions of specimens from varied sources is very marked. This is also shown in a much clearer manner in the results reported herein. Another mineral thought to be the main constituent of certain samples of bentonite is also a hydrated alumino-silicate, montmorillonite. It has been assigned the formula $\text{H}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 4 \text{ SiO}_2 \cdot n\text{H}_2\text{O}$. Altogether, the situation regarding the exact nature of bentonite is obscure.

Five samples of bentonites⁵ from different sources, some of which had been specially purified, were treated as described (method 2), and the equilibrium constants for the Ca-Mg exchange reaction determined. The results are given in table 2.

Two interesting features are shown by the results; 1. The various samples possess a wide range of base exchange capacity, from 46.4 to 104.2 milliequivalents per 100 gm.; 2. The equilibrium constants for all samples are identical within the limits of experimental accuracy. Samples 4 and 5 were very small in amount, and, hence, the experimental error in the results from these was considerably greater than with the other three samples. The mean value for K for the five samples is $1.12 \pm .017$. This value is in very good agreement with the values obtained for other samples of bentonite which have been examined from time to time, and also with the sample of Hawaiian soil from which the organic matter was completely removed.

COMPOSITION OF ACTIVE ALUMINO-SILICATE IN BENTONITE

The final problem was, then, to determine the composition of the active alumino-silicate present in bentonite. Sample 1 was chosen for this purpose by reason of its high base exchange capacity and apparent freedom from iron compounds. The method employed for the decomposition of the mineral was essentially that already outlined for the soil extraction. A sample of approximately 2.5 gm. was taken, and leached with 0.05 N HCl to remove easily soluble free Al_2O_3 .⁶ Extraction of the residue with a 10 per cent Na_2CO_3 solution removed any colloidal silicic acid present. The sample was then boiled with 250 cc. of 0.2 N HCl, under reflux, for 7 hours. The filtered extract was analyzed for SiO_2 , Al_2O_3 , and Fe_2O_3 . The remaining free silicic acid was finally removed from the residue by treatment with a 10 per cent solution of Na_2CO_3 , and the extracted SiO_2 determined. The insoluble residue was taken for a determination of the residual base exchange capacity. Even after the prolonged treatment with acid, the residue was capable of retaining 66.4 milliequivalents of exchangeable Ca per 100 gm. In this respect, it will be seen that the soil sample treated above closely resembles this sample of bentonite; the active alumino-silicate which each contains is resistant to the action of boiling acid, as compared with the true zeolites.

In order to hasten the decomposition process, the use of a stronger acid was tried. The insoluble residue from the previous treatment was boiled with 250 cc. of N HCl for 12 hours. The extract was filtered off and the silicic acid removed from the residue with Na_2CO_3 as before. The insoluble material now possessed no capacity for base retention.

A further independent sample of bentonite from California was subjected to extraction with N HCl for 18 hours, and the liberated silicic acid was taken

⁵ The bentonites were received through the courtesy of Dr. Clarence S. Ross of the U. S. Geological Survey.

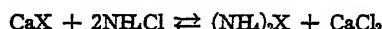
⁶ About 0.2 per cent of Al_2O_3 was removed by this treatment.

out as before. This treatment was sufficient to destroy the base exchange property entirely. The analyses of the extracts from these two samples are given in table 3.

The molecular proportions in which SiO_2 , Al_2O_3 , and combined water were present agree well for these two samples. In employing the above method of decomposition of the alumino-silicate, it was assumed that no extraneous minerals would be decomposed at the same time. There is no real justification for this supposition, and one can but judge the method by the results obtained. The decomposition of a small proportion of some other mineral of a lower SiO_2 to Al_2O_3 ratio would account for the departure from the exact 6 to 1 ratio. The small amounts of Fe_2O_3 extracted would seem to be present as the free oxide, and, hence, would take no part in the constitution of the active mineral destroyed. The combined water, as given in the table, was the loss on ignition of material which had been dried at 105°C. Bentonite is highly hygroscopic, and this sample 2 readily absorbs up to 15 per cent H_2O on exposure to the atmosphere.

The one point which required clarification in the above analyses was the proportion of base held in combination by the active alumino-silicic acid. The molecular ratios of base to Al_2O_3 to SiO_2 for the zeolites are 1 to 1 to x , where x may be 2, 3, 4, or 6; in other words, they are salts of a dibasic alumino-silicic acid. It was first assumed that the alumino-silicate of the bentonite was also a salt of a dibasic acid, but the results obtained in the above extraction threw some doubt on this assumption.

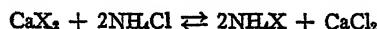
Fortunately, the theory for the kinetics of the exchange equilibrium is very useful in the determination of the basicity of the acid involved in the reaction. Where cations of the same valence take part in the exchange, this factor does not enter, but when the exchange between, say, NH_4^+ ions and Ca^{++} ions is under consideration, the true basicity of the acid must be known, for, supposing the acid to be dibasic, the reaction will be represented:



and

$$K_1 = \frac{(\text{NH}_4^+)^2 (\text{CaX})}{(\text{NH}_4)_2\text{X} (\text{Ca}^{++})} \quad (B)$$

If the acid be monobasic, the calcium salt will be represented as CaX_2 , and then:



which gives

$$K_2 = \frac{(\text{NH}_4^+)^2 (\text{CaX}_2)}{(\text{NH}_4\text{X})^2 (\text{Ca}^{++})} \quad (C)$$

On substituting, then, the values obtained in a series of equilibrium studies (as described under method 1), in each of these equations, one or the other, but not both, should give a constant value for K . An experiment of this kind was performed with the sample of soil which had been slowly oxidized in the electric furnace. The results are given in table 4.

The constancy of the values for K_2 as against those for K_1 offers very strong evidence in favor of the monobasicity of the alumino-silicic acid. This would

TABLE 1
Ca-Mg equilibria in exchange reaction with a Hawaiian subsoil saturated with calcium

TRIAL NUMBER	TOTAL REPLACEABLE Ca IN 83.3 GM. MATERIAL*	EQUILIBRIUM CONCENTRATIONS				CONSTANT K
		CaCl ₂	MgCl ₂	CaX	MgX	
	milliequivs.	milliequivs.	milliequivs.	milliequivs.	milliequivs.	
1	6.68	2.88	3.03	3.78	2.88	1.40
2	6.68	3.03	3.60	3.65	3.03	1.39
3	6.68	3.24	4.35	3.44	3.24	1.42
4	6.68	3.44	5.13	3.24	3.44	1.40
5	6.68	3.60	5.84	3.08	3.60	1.39
6	6.68	3.73	6.65	2.95	3.73	1.43
7	6.68	3.85	7.57	2.83	3.85	1.45
8	6.68	3.96	8.27	2.72	3.96	1.44

* Weight of soil per litre of suspension.

TABLE 2
Equilibrium constants for the Ca-Mg exchange reaction, with different samples of bentonite

SAMPLE NUMBER	MINERAL DESCRIPTION AND SOURCE	TOTAL EXCHANGE CAPACITY PER 100 GM.	CONSTANT K
		milliequivs.	
1	Bentonite—Montmorillonite from Rideout, Utah	97.7	1.14
2	Bentonite—from Mexico	103.3	1.11
3	Bentonite—Montmorillonite. Colloidal type. Wyoming	104.2	1.10
4	Bentonite—Potash-bearing clay. Alabama	46.4	1.17
5	Bentonite—Beidellite from Fairview, Utah	55.6	1.09

require a ratio of base to Al₂O₃ of 1 to 2; but the values obtained give only 0.75 to 2. It is felt that this apparent discrepancy may be accounted for in part by each of the following factors: (a) The decomposition of alumino-silicates in the bentonite, other than that active in base exchange or solution of a small amount of free Al₂O₃, probably present, would increase the amount of Al₂O₃ extracted, and decrease the relative molecular proportion of base to Al₂O₃. (b) Bentonite has been formed in nature under conditions similar to those effecting soil formation and has been subjected to more or less leaching. The

resulting product does not exhibit a noticeable degree of acidity, although about 3 milliequivalents of free acetic acid per 100 gm. of bentonite were obtained on leaching a sample with 0.5 N barium acetate solution. However, this method is not a satisfactory one by which to determine the "degree of unsaturation" of such an alumino-silicate. The alumino-silicic acid is undoubtedly a weak one, and its "neutral" salts would suffer considerable hydrolysis. For the true zeolites, a suspension of powdered, unweathered zeolite has a pH of 9-10; if such a compound be leached until it reaches a pH value of 7,

TABLE 3

Material of bentonite soluble and insoluble in normal hydrochloric acid and 10 per cent sodium carbonate solution, and total base exchange capacity

	SAMPLE FROM RIDGEOUT, UTAH		SAMPLE FROM CALIFORNIA	
	gm.	molar proportions	gm.	molar proportions
SiO ₂	1.1458	5.82	1.0658	5.43
Al ₂ O ₃	0.3342	1.00	0.3346	1.00
Fe ₂ O ₃	0.0155	0.03	0.0420	0.08
H ₂ O (combined).....	0.2300	3.90	0.2306	3.92
Insoluble residue.....	0.3785	0.1478
Total exchange capacity as Ca.....	0.0694	0.38	0.0640	0.35

TABLE 4
Ca-NH₄ equilibria in exchange reaction with oxidized Hawaiian soil

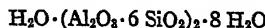
TRIAL NUMBER	TOTAL REPLACEABLE Ca PER 62.5 GM. SOIL*	EQUILIBRIUM CONCENTRATIONS				K ₁ CALCU- LATED ON BASIS DIBASIC ACID	K ₂ CALCU- LATED ON BASIS MONO- BASIC ACID
		CaCl ₂	NH ₄ Cl	Ca-alumino- silicate	NH ₄ -alumino- silicate		
milliequivalts.	milliequivalts.	milliequivalts.	milliequivalts.	milliequivalts.	milliequivalts.		
1	9.14	1.50	2.40	7.64	1.50	19.5	13.0
2	9.14	2.00	3.80	7.14	2.00	25.8	12.9
3	9.14	2.46	5.27	6.68	2.46	30.7	12.5
4	9.14	2.81	6.83	6.33	2.81	37.4	13.3
5	9.14	3.15	8.33	5.99	3.15	41.9	13.3
6	9.14	3.50	9.93	5.64	3.50	45.4	13.0

* Weight of soil per liter of suspension.

considerable amounts of base will have been replaced by hydrogen, and yet the residue is "non-acid." Unfortunately, we have no satisfactory method of determining this degree of unsaturation. As an approximation to the true value, the absorption of calcium from a solution of Ca(OH)₂ was determined. This method is open to the objection that secondary reactions might be brought about under these conditions; for example, free SiO₂ and Al₂O₃ might dissolve in the alkali and reprecipitate as zeolitic alumino-silicates, thus unduly increasing the apparent base absorption. However, a determination carried out in this manner with bentonite gave an absorption of 0.11 per cent CaO.

This would give the total exchangeable base per mole of Al_2O_3 a value of 0.98, which agrees very well with the requirement of the postulated formula.

Summing up, then, the evidence would indicate that the chemical formula of alumino-silicic acid, whose salts confer upon the soils and samples of bentonite tested the property of base exchange, is:



The salts would then be of the general formula:



So far as can be ascertained, no such compound is described in the literature, but probably many of the properties which have been ascribed to beidellite and montmorillonite are characteristic of this mineral, for, from the above formula, the total exchangeable base held by 100 gm. of this compound would be 180 milliequivalents for the Ca salt. Allowing for the acidic hydrogen in the natural product, we might safely conclude that the two samples examined contained about 80 per cent of the active alumino-silicate (calculated on the sample dried at 105°C.); the remaining 20 per cent may be assumed to be made up of undecomposed rock fragments and other products of rock weathering.

By thoroughly leaching a sample of bentonite with 0.1 N HCl and washing the residue with water until free from chloride, a highly colloidal residue was obtained. Its acidic properties were very marked. A suspension of one part in ten of water showed a pH of 2.73, when measured by the quinhydrone electrode, and the solid material gave a strongly "acid" taste when placed on the tongue. A suspension was readily titratable with a solution of alkali. Yet this compound, in common with the active alumino-silicic acids obtained in a similar manner from the samples of zeolites previously described, is quite insoluble in water.

It is hoped that further tests will be made to establish definitely the identity of the silicate present in the bentonite and that active in the soil. This will be done on samples from various sources, formed under a wide range of climatic conditions, and from varied parent materials.

It is not proposed to speculate at this time regarding the possible parent mineral from which the active alumino-silicate is formed during weathering. Presumably, it is an intermediate decomposition product in the weathering of primary alumino-silicates, during the degradation process of which the end products are Al_2O_3 and SiO_2 . The fact that the Al_2O_3 to SiO_2 ratio appears to be identical with that of the potassium and sodium feldspars suggests that these may be the parent minerals. Further work should throw some light on this possibility.

SUMMARY

In a previous publication there was reported a mass action equation which describes the heterogeneous equilibria involved in base exchange of zeolites

and soils, and which thus permits the derivation of a constant K , the value of which is characteristic for each compound involved in base exchange reactions. Continuing this work, an attempt was made by application of this constant to establish the identity and composition of the material involved in base exchange of soils. Separation of this material by specific gravity methods and by use of solvents was also attempted. The results of these investigations are as follows:

1. The base exchange material of soils is confined largely to the clay fraction and seems to be so intimately mixed with other colloidal material that it is impossible to separate it by specific gravity methods. Separation by the use of solvents is complicated, because of the solution of other materials which obscure the results.

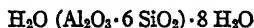
2. By employing the constants derived according to the base exchange equilibrium theory, as developed by the writer, it was possible to identify active alumino-silicates from different sources. The equilibrium constant seems to be characteristic of each compound involved in base exchange.

3. The soil from which the active organic matter had been completely removed by gentle ignition gave a value for K agreeing very closely with samples of a clay material—bentonite—and differing markedly from the values found for the true zeolites tested. This suggests that the inorganic compounds involved in base exchange of soils and bentonite are identical.

4. Bentonite is a mixture of at least two minerals, which are very difficultly separated by mechanical means, because of the colloidal properties of the substance.

5. It was found possible to decompose the active mineral of bentonite by boiling for 18 hours with a normal solution of HCl. The liberated silicic acid was then extracted with a 10 per cent solution of Na_2CO_3 . The analyses of these extracts showed that the ratio of Al_2O_3 to SiO_2 was almost 1 to 6.

6. By further consideration of the base exchange reaction for cations of different valence, it was shown that the active alumino-silicic acid was monobasic, and when due allowance was made for the unsaturation of the compound, the analyses calculated from the free acid agreed fairly well with the formula:



7. By leaching a sample of bentonite with 0.1 N HCl and washing the sample with water, the free acid was prepared. This acid suspended in water gave a pH of 2.73.

8. It is suggested that the compound described is of widespread occurrence in soils and, for those which are non-alkaline, is possibly the predominant if not the only mineral in their inorganic exchange complex.

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BOOK REVIEW

The Microbiology of Cellulose, Hemicelluloses, Pectin, and Gums. By A. C. THAYSEN and H. J. BUNKER. Oxford University Press, London, 1927. Pp. 363.

Because of the great interest during the last few years in cellulose decomposition in soil, this book should be of especial interest to soil microbiologists. The subject is treated largely from the purely microbiological viewpoint, but the process itself has received some consideration. Although the authors are not pedologists, they give considerable space to the decomposition of these carbohydrates by soil microorganisms.

The first chapter gives a very brief summary of our present knowledge of the chemistry of these materials. Because of the lack of space the discussion is inevitably sketchy and incomplete, but it does give a general idea and corrects many of the common misconceptions. The second chapter deals with the importance of the microbial decomposition process and points out that it is of interest theoretically as well as practically.

The principal part of the book deals systematically with the various micro-organisms which have been described as decomposing celluloses, pectins, gums, and hemicelluloses. Although this section is written critically there are several surprising errors and omissions. For instance, although it is certain, on Omelianski's own admission, that he did not work with pure cultures, this work is given prominence far out of keeping with its present value. Certainly the recent work of Khouvine at the Pasteur Institute, who undoubtedly worked with a pure culture, isolated by herself, has a more exact value than the original work of the Russian investigator, except in a historical way. Probably the fact that the authors had apparently consulted only the abstract of Khouvine's paper, published in the Pasteur Institute annals, rather than the original thesis, explains their attitude toward this very important piece of work.

The long controversy over the work of Kellerman, McBeth, Scales, and Smith, on aerobic cellulose decomposers, could have been brought to a close in this book, since there should have accumulated enough data by this time to show that these workers were dealing with cellulose decomposing organisms in pure culture, although possibly not very important ones. It is surprising to read on page 49 that von Gescher's "observations show clearly that the American workers were dealing with mixed cultures," when it can easily be verified that the cultures are pure by obtaining them from the investigators themselves, or from a culture museum, as the reviewer has done. Likewise the statement that the one convincing experiment, namely, a quantitative determination of the amount of cellulose decomposed, has not been carried out, is astounding,

since it is with one of these groups that Waksman and Heukelekian (*Act. IV. Conf. Pedologie*, 1924) determined by a direct chemical analysis of the residual cellulose, that 29 per cent of the filter paper used was decomposed in 42 days. This also disposes of the objection of von Gescher that the cultures contained cellulose decomposing impurities which rapidly died out, for the cultures were ten years old when the "really convincing experiment" was done.

The authors of this monograph criticize Heukelekian's argument that molds are of prime importance in the decomposition process in the soil, because no account was taken of the cellulose decomposing bacteria which do not grow on ordinary media. This criticism is undoubtedly justified and could equally well be made against a paper by the reviewer (with Waksman) which was criticized also by Winogradsky on the same ground. However, Dubos, working in the same laboratory by different methods, has recently given equal importance to the bacteria, although fungi are considered of sole importance in normal, humid, acid soils.

Thaysen and Bunker give a very incomplete résumé of actinomycetes which decompose cellulose, having cited very few of the papers on that subject since 1918. It is evident that they are not at all familiar with the group, otherwise the taxonomic system of Ørskov would hardly have been used. None of the species described in *Soil Science* since 1918 has been included, and the bulk of the American literature on these interesting soil organisms is ignored. It is doubtful whether a determination of species is of much value, because of their variability, but as long as some species are described in detail, the rest of them, most of which, incidentally, have been more completely described in the literature, should also have been included.

The systematic treatment of fungi decomposing cellulose is rather well compiled, although some of the important papers on this subject are not included. This is surprising since they have often been cited and are among the best on the subject. The work of Daszewska 1913, Mütterlein 1913, Waksman 1916, and Heller 1917, especially should have been included. The description of species is hardly worth while in a book of this sort, for the lack of space makes complete descriptions impossible. A careful taxonomist will refer to monographic systematic treatments of the particular group in which he is interested, to original descriptions, or to type strains. Others can get along without any description at all.

The importance of the nitrogen supply in cellulose decomposition is touched upon in connection with the important work of Barthel and his associates in Sweden. Thaysen and Bunker have apparently no conception of the importance of nitrogen in the resynthesis by fungi of nearly half of the cellulose decomposed. These microbial cells contain five to ten per cent of nitrogen. An understanding of this would have simplified the discussion of the decomposition in soil and of the well-known process of composting in the preparation of "artificial farmyard manure," recently patented in Great Britain. Also it is almost inconceivable that the use of the rather overworked term "carbon-

"nitrogen ratio" should have been avoided, but the authors have accomplished this feat without, however, having explained the principle.

The book, as a whole, has something to recommend it. Soil microbiologists should have access to it for the very extensive bibliography and for its treatment of the chemistry of the substances in question, if for nothing else. The preface bears the date 1925, but the title page, 1927. This delay on the part of publishers tends to make a book out of date almost before it leaves the press. The systematic portion on fungi, as far as it goes, and the discussion of the decomposition of fibers, fabrics, wood, paper, pulp, etc., are of interest, and are subjects upon which a soil scientist is not likely to have a very thorough knowledge. However, one who is at all familiar with the subject of cellulose decomposition will find the book disappointing. A good critical monograph on microbial decomposition of cellulose is very much needed. The chapters in the books of Sir John Russell and of Professors Pringsheim and Waksman, still remain the best on the subject.

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AN APPARATUS FOR THE SUPERFICIAL EXAMINATION OF ROOTS AND NODULES

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In testing cultures of legume bacteria for efficiency in nodule production, the test plants are usually grown in bottles containing sand, moistened with a nutrient solution. The final examination includes observations on the nodules and roots and the counting or, in some cases, the estimating, of the numbers of nodules produced. For this purpose the plants are removed from the bottles, shaken carefully to throw off the major portion of the clinging particles of sand and then rubbed *very gently* under water to remove the remaining grains. For purposes of observation and counting the nodules and roots are better observed when floated in water¹ in a pan with a white lining or, preferably, in a tank with a glass bottom through which light may be directed. Such a piece of apparatus has been designed and used in this laboratory and has proved to be very satisfactory.

This device is, essentially, a reinforced copper tank measuring $25\frac{1}{2} \times 27 \times 7\frac{1}{2}$ centimeters² with a clear, plate glass bottom fastened into place by means of a cement composed of litharge and spar varnish. These ingredients are mixed to a thick paste, all lumps rubbed out, and the mixture allowed to stand 12 hours before being used. The outside of the glass bottom is ruled into squares of 1×1 cm., with a red wax pencil (or these squares may be etched permanently with hydrofluoric acid), for the purpose of measuring the length of the plants while the rest of the examination is being made. The tank is mounted in a wooden framework, from which it can readily be removed. This framework is equipped with two adjustable arm rests and with a light compartment wired to accommodate six 25-watt frosted tubular bulbs. The over-all length of the apparatus is 92 cm., and the height of the light compartment is $10\frac{1}{2}$ cm. For greater diffusion of the light, a piece of ground glass is usually placed on the

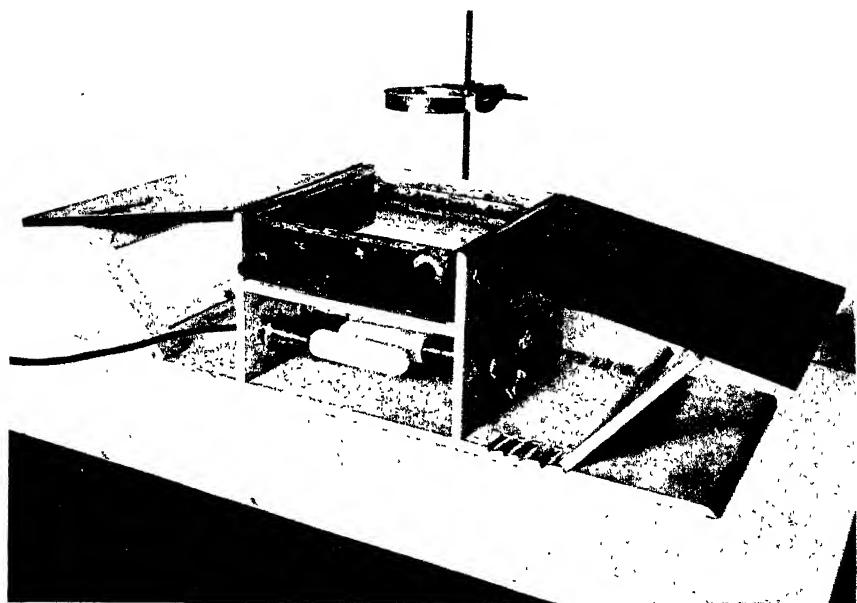
¹ While making such examinations, it is necessary to immerse the hands in the water. When the work continues for several hours the tips of the fingers shrivel. This disagreeable condition can be avoided by the use of rubber gloves, but, as these interfere to some extent with the movement of the fingers, they are not desirable. It has been found, however, that by occasionally coating the hands with a rather hard cup grease, this shriveling is eliminated and a satisfactory manipulation of the fingers is possible.

² These dimensions may, of course, be varied, with accompanying changes in the framework, in order to accommodate larger plants.

framework between the bottom of the tank and the light compartment. A ground glass bottom may, of course, be cemented into the tank itself, but the above arrangement allows a greater flexibility in the adjustment of light intensity. An ordinary reading glass is mounted over the tank by means of an adjustable rod moving through rings soldered to a side of the tank and provided with set screws. A clamp holder fixes the lens in place on the rod and allows for angular adjustment. By the use of this, the roots and nodules can be more closely examined and very small nodules more readily counted. Two openings are provided on a side of the tank, one near the left hand bottom and the other near the right hand top, in case it is desired to maintain a constant flow of water through the tank in order to prevent excessive turbidity. The interior of the light compartment should be painted a glossy white and the remainder of the woodwork, a flat black. The complete apparatus is shown in plate 1.

This device has proved an efficient aid in the examination of legume plants and nodules and in the counting of the nodules.³

³Appreciation is due C. C. Wilson and F. M. Grant of the department's mechanical shops for their suggestions in the designing and assembling of this apparatus.



THE APPARATUS DESIGNED FOR THE SUPERFICIAL EXAMINATION OF ROOTS
AND NODULES

EXCHANGEABLE CATIONS IN SOILS AS DETERMINED BY MEANS OF NORMAL AMMONIUM CHLORIDE AND ELECTRODIALYSIS

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Exchangeable cations in soils have been determined, in large measure, by means of extraction with a weak acid or with a neutral-salt solution. More recently electrodialysis has been employed for this purpose. It will not be necessary, at this time, to discuss the development of these methods or the principles involved, nor will an attempt be made to review the literature on cationic exchange in soils, except as it bears directly on the results of the present investigation.

The work here reported is concerned with the quantity of certain cations in a number of soils, collected from various localities in New York, as determined by extraction with $N\text{ NH}_4\text{Cl}$ and by electrodialysis. In selecting soils for study, care was exercised that each should be characteristic of its particular type. In some instances soils of the same type were collected from different counties in order that a comparison of their exchangeable cations might be made.

DESCRIPTION OF SOILS

Twelve soils, of six different series, were employed for study. To obviate a lengthy description of these soils, a number of facts concerning them are brought together in table 1. Four of the soil types listed in the table originated from the weathering of glacial-till and two of them from the decomposition of glacial-lake clay. The soils of the first three types are represented by samples from each of two counties, while the Volusia silt loam is represented by four samples from three different counties. The soils designated as Dunkirk silty clay loam and Wooster gravelly silt loam, of which one sample is shown for each, were sampled to a depth of 8 inches. All of the other soils were sampled to a depth of 12 inches. In preparation for analysis the soils were air-dried and passed through a 1 mm. sieve.

METHODS EMPLOYED

Exchangeable cations were determined by means of the NH_4Cl method, as modified by Kelley and Brown (3), and by electrodialysis using the two-com-

TABLE 1
The soils of the investigation

SOIL	LOCATION	PARENT MATERIAL		COLOR	SUBSOIL	TOPOGRAPHY	TERRAIN
		Nature	Deposition				
Dutchess silt loam	Dutchess Co. Orange Co.	Slate quartzite	Glacial till	Brown	Open friable	Rolling	Fair
Ontario loam	Monroe Co. Oneida Co.	Shale sandstone lime-stone	Glacial till	Dark brown	Open friable	Rolling	Good
Vergennes clay	Jefferson Co. Washington Co.	Mixed material lime-stone dominant	Lacustrine	Grayish brown	Compact	Flat	Good
Volusia silt loam	Allegany Co. Cortland Co. Tompkins Co. (Cayuta) Tompkins Co. (Turkey Hill)	Shale sandstone	Glacial till	Brown	Compact	Rolling	Poor
Dunkirk silty clay loam	Tompkins Co.	Mixed material lime-stone dominant	Lacustrine	Brown	Compact	Undulating	Fair
Wooster gravelly silt loam	Cayuga Co.	Shale sandstone conglomerates	Glacial till	Brown	Open friable	Rolling	Good

partment-Pyrex cell devised by Bradfield (2). The modified NH₄Cl method consists essentially in first digesting, and later leaching, a soil with a solution of *N* NH₄Cl. A portion of the resulting filtrate is then evaporated to dryness on a steam bath in the presence of concentrated HNO₃, which decomposes the NH₄Cl present. This simplifies considerably the subsequent determinations for cations by standard methods of analysis.

Ten grams of soil were used for electrodialysis. A direct current of 110 volts was employed, which was regulated by means of a sliding-contact rheostat. An anode of platinum foil 1 x 5 cm. and a cathode of perforated-sheet nickel 6 x 11 cm. were used. The latter was cylindrically shaped to encircle an alundum thimble 3.2 x 12.7 cm., RA—84 dense, which served as a membrane. The apparatus used in the investigation is shown in plate 1. It is similar in design to the one described by Bradfield (2). The amperage and the length of time to which the soils were subjected to dialysis varied with the experiments.

Hydrogen-ion concentrations were ascertained potentiometrically, using a quinhydrone electrode.

EXCHANGEABLE CATIONS

The quantities of calcium, magnesium, and potassium brought into solution, when the soils of the investigation were leached with *N* NH₄Cl or electrodialyzed, are shown in table 2. The values are expressed in milligram equivalents per 100 gm. of air-dry soil.

The soils of the Ontario and the Vergennes series, the most productive of those studied, were found to contain the largest quantities of exchangeable calcium. The values shown for these series do not differ greatly for soils of the same type collected in different counties. But this does not hold for the soils of the Dutchess series. The sample of soil from Dutchess County contained much more calcium in an exchangeable form than did the one from Orange County. The four soils of the Volusia series varied considerably in this constituent. Of this series, the soil from Cayuta, having the largest quantity of exchangeable calcium, is known to be a more fertile soil than the one from Turkey Hill shown as having the smallest quantity. Although the fertility of the Dunkirk silty clay loam soil is considered to be greater than that of the Volusia silt loam soil, the former was not found to contain more exchangeable calcium than the latter. It is usually held that the soils of the Wooster series are more fertile than those of the Volusia series. A comparison of the exchangeable calcium in each of these does not show this to be the case, if a larger quantity of this constituent is a measure of greater fertility.

Since all of the soils were not sampled to the same depth, and since the number of soils analyzed was small, the above comparisons may not be warranted. However, the soils which were found to contain the largest quantities of exchangeable calcium, those of the Ontario and the Vergennes series, are undoubtedly the most fertile of the soils examined, and tests with the soil which

was found to contain the smallest quantity of exchangeable calcium, the Dutchess silt loam from Orange County, have shown it to be exceedingly infertile. Thus, it appears that the extent to which calcium is held in exchangeable form in these soils is in some measure an index to their fertility.

A comparison of the values for exchangeable calcium, as determined by the two methods employed, shows them to be in close agreement; however, the values obtained by means of electrodialysis are smaller, with two exceptions, than are those obtained by means of extraction with $N\text{ NH}_4\text{Cl}$.

Each soil was found to contain a smaller quantity of exchangeable magnesium than of exchangeable calcium. But those soils containing the largest

TABLE 2

Exchangeable cations as determined by means of extraction with normal NH_4Cl and electrodialysis

SOIL	MILLIGRAM EQUIVALENTS PER 100 GM. OF AIR-DRY SOIL						
	Calcium NH ₄ Cl extrac- tion	Magnesium Electrodialysis	Potassium NH ₄ Cl extrac- tion	Total Electrodialysis	Potassium Electrodialysis	Calcium NH ₄ Cl extrac- tion	Total Electrodialysis
Dutchess silt loam, Dutchess Co.....	5.94	5.29	1.38	0.65	0.55	0.59	7.87
Dutchess silt loam, Orange Co.....	2.16	1.80	0.90	0.33	0.93	0.97	3.99
Ontario loam, Monroe Co.....	11.20	10.85	3.67	0.98	0.56	0.59	15.43
Ontario loam, Oneida Co.....	10.00	10.61	2.33	1.13	0.55	0.52	12.88
Vergennes clay, Jefferson Co.....	10.93	10.96	9.30	2.33	2.18	0.96	22.41
Vergennes clay, Washington Co.....	11.45	9.86	6.50	1.46	1.74	0.83	19.69
Volusia silt loam, Allegany Co.....	7.57	6.57	1.56	0.90	0.85	0.71	9.98
Volusia silt loam, Cortland Co.....	6.12	5.66	2.46	1.07	0.90	0.61	9.48
Volusia silt loam, Tompkins Co. (Cayuta)	8.96	8.58	1.75	1.04	0.75	0.62	11.46
Volusia silt loam, Tompkins Co. (Turkey Hill).....	5.04	4.24	1.60	0.98	0.68	0.63	7.23
Dunkirk silty clay loam, Tompkins Co....	6.67	4.63	1.37	0.93	0.50	0.64	8.54
Wooster silt gravelly loam, Cayuga Co....	4.47	3.36	1.31	0.66	0.47	0.55	6.25
							4.57

quantities of calcium in this form also contain the largest quantities of exchangeable magnesium. The converse of this was also found. The outstanding feature in regard to exchangeable magnesium is the discrepancy in the values obtained by means of the methods employed. Considerably less magnesium was recovered by electrodialysis. This is especially noticeable in the case of the Ontario loam soil from Monroe County and the soils of the Vergennes series in which the quantities of exchangeable magnesium are large.

Exchangeable potassium was found to be low in the soils as compared with exchangeable calcium and magnesium. The methods of analysis are seen to agree for potassium when it is present in small quantities, but when it exists in comparatively large quantities less was extracted by electrodialysis than by

treatment with $N\text{ NH}_4\text{Cl}$. In this respect its behavior is similar to that of magnesium. This phase of the subject will be discussed presently.

In table 3, when the relative proportions of the three exchangeable cations are presented, calcium is shown to be predominant. This is in agreement with the findings of a number of investigators, working with a large variety of soils, the data for some of which have been assembled by Smith (7). On the other hand, the relative proportions of magnesium and potassium, as shown in table 3 are somewhat higher than are those which have been generally reported. It may be said, however, that the soils of the present investigation, are rather high in both magnesium and potassium.

TABLE 3

Relative proportions of exchangeable cations as determined by means of extraction with normal NH_4Cl and electrodialysis

SOIL	CALCIUM		MAGNESIUM		POTASSIUM	
	NH_4Cl extrac- tion	Elec- trodi- alysis	NH_4Cl extrac- tion	Elec- trodi- alysis	NH_4Cl extrac- tion	Elec- trodi- alysis
Dutchess silt loam, Dutchess Co.....	75.5	81.0	17.5	10.0	7.0	9.0
Dutchess silt loam, Orange Co.....	54.1	58.1	22.6	10.6	23.3	31.3
Ontario loam, Monroe Co.....	72.6	87.4	23.8	7.9	3.6	4.7
Ontario loam, Oneida Co.....	77.6	86.5	18.1	9.2	4.3	4.3
Vergennes clay, Jefferson Co.....	48.8	76.9	41.5	16.4	9.7	6.7
Vergennes clay, Washington Co.....	58.2	81.2	33.0	12.0	8.8	6.8
Volusia silt loam, Allegany Co.....	75.9	80.3	15.6	11.0	8.5	8.7
Volusia silt loam, Cortland Co.....	64.6	77.1	25.9	14.6	9.5	8.3
Volusia silt loam, Tompkins Co. (Cayuta)....	78.2	83.8	15.3	10.2	6.5	6.0
Volusia silt loam, Tompkins Co. (Turkey Hill) ..	68.8	72.4	21.9	16.8	9.3	10.8
Dunkirk silty clay loam, Tompkins Co.....	78.1	74.7	16.0	15.0	5.9	10.3
Wooster gravelly silt loam, Cayuga Co.....	71.5	73.5	21.0	14.5	7.5	12.0

DISCUSSION OF METHODS

It was shown in the preceding experiment that approximately equivalent quantities of exchangeable calcium were extracted from soil with $N\text{ NH}_4\text{Cl}$ and by electrodialysis. Similar comparisons made by Mattson (4), Bradfield (2), and Odén (6), each using a different type of electrical cell have led to the same conclusion. This relationship appears to hold, regardless of whether the quantity of exchangeable calcium is large or small. A similar relationship was not found by the writer with reference to exchangeable magnesium, and in some cases, with reference to exchangeable potassium. Attention has already been called to the fact that electrodialysis released a lesser quantity of these cations than did extraction with $N\text{ NH}_4\text{Cl}$, especially when they were present in the soils in greater amounts. For example, electrodialysis extracted from the Vergennes clay soil from Jefferson County only about 25 per cent as much magnesium, and about 44 per cent as much potassium, as was extracted with $N\text{ NH}_4\text{Cl}$.

To ascertain whether the NH_4Cl employed in the work was responsible for the disagreement in the methods, several lots of the material from different sources were used for extraction. All of them gave concordant results. When made with distilled water, N NH_4Cl has a reaction of about pH 5.0. Adjusting this solution to a reaction of pH 7.0, by means of NH_4OH , did not alter the quantities of exchangeable magnesium and potassium extracted from the soils of the investigation.

The electrodialysis values shown in table 2 were obtained by electrodialyzing the soils for 8 hours at an amperage of about 100 milliamperes. At times the amperage was somewhat lower but it was never greater than 200 milliamperes. Usually about 1 liter of the diffusate was obtained during electrodialysis.

It appeared likely that more of the magnesium and potassium might be recovered in the diffusates if a larger current was passed through the cell. Consequently 10 gm. of the Vergennes clay soil from Jefferson County, which was found, by the N NH_4Cl -extraction method, to contain the largest exchangeable

TABLE 4

Cations extracted from the Vergennes clay soil from Jefferson County by treatment with normal NH_4Cl and by electrodialysis

METHOD	MILLIGRAM EQUIVALENTS PER 100 GM. OF AIR-DRY SOIL		
	Calcium	Magnesium	Potassium
Electrodialysis, reduced current.....	10.96	2.33	0.96
Electrodialysis, full current.....	11.55	10.70	2.17
Extraction with N NH_4Cl	10.93	9.30	2.18

quantities of these cations, was subjected to electrodialysis with no resistance in the circuit. Dialysis was rapid. At the end of 8 hours, when it was discontinued, about 4 liters of the diffusate had been collected. The amperage was not high, since the resistance of the cell was sufficiently great to maintain it at a low figure. It was never above 300 milliamperes and it decreased, as dialysis was continued, to a value of approximately 50 milliamperes. The cell became noticeably warm, the outer compartment reaching a temperature of 42°C .

The results of this test are shown in table 4, which also contains, for comparison, the data which were obtained by the electrodialysis of the same soil when a rheostat was used in the circuit and those which were secured by means of N NH_4Cl extraction. The quantities of magnesium and potassium extracted when the full current was employed were considerably greater than were those previously obtained by means of a reduced current. But they are seen to agree rather closely with the values shown for the N NH_4Cl method. Unlike magnesium and potassium, the presence of calcium in the diffusate resulting from the full-current dialysis was increased only slightly.

FRACTIONAL DIALYSIS

Continuing the study of the removal of these three cations, together with iron and aluminum, by means of electrodialysis, the soils of the Vergennes series, both of which are relatively high in exchangeable cations, were subjected to fractional dialysis. They were electrodialyzed for 32 hours, the diffusates for each 8-hour period being collected and analyzed separately. The procedure was similar to that of the first experiment, the dialysis being conducted under the influence of a reduced current at an amperage of about 50 milliamperes. Approximately one liter of the diffusates was collected during each 8-hour period.

The concentrations of the several cations in the different fractions are recorded in table 5. The first fraction contained all of the exchangeable cal-

TABLE 5
Cations extracted from soils by fractional electrodialysis

SOIL	FRACTION	MILLIGRAM EQUIVALENTS PER 100 GM. OF AIR-DRY SOIL			
		Fe + Al	Ca	Mg	K
Vergennes Clay, Jefferson Co.	A	0.74	11.16	2.01	0.87
	B	1.47	0.21	2.48	0.37
	C	1.65	0.00	0.47	0.26
	D	1.00	0.00	0.40	0.24
	Total	4.86	11.37	5.36	1.74
Vergennes Clay, Washington Co.	A	0.53	9.91	1.22	0.76
	B	1.56	0.00	0.97	0.26
	C	1.03	0.00	0.29	0.18
	D	1.12	0.00	0.14	0.19
	Total	4.24	9.91	2.62	1.39

cium extracted from the soil from Washington County and practically all of that recovered from the soil from Jefferson County. Magnesium and potassium were found in all of the fractional diffusates for each of the soils but the quantities became less as dialysis was continued. The total quantities of magnesium and potassium removed respectively, during the 32 hours of dialysis, were less than those extracted with $N\text{ NH}_4\text{Cl}$ or those recovered by means of full-current dialysis during a period of eight hours. Iron and aluminum were found in all of the fractions. The sum of these cations was smaller in the first fraction than in subsequent fractions and showed little tendency to decrease in quantity as the process of dialysis was prolonged.

Electrodialyzing the colloidal material of a Sharkey clay soil in successive fractions, Mattson (4) found most of the calcium and potassium removed during the entire process to be present in the first fraction. Conversely, iron, aluminum, and magnesium were present in the first fraction as traces only,

increasing in amount with each succeeding fraction. In principle, these results agree with those of the present paper, especially with reference to calcium and magnesium. Certain differences are to be expected, since, in the case just cited, colloidal material only was dialyzed.

DIFFERENCES IN CATIONIC BEHAVIOR

There appears to be a distinct difference in the manner in which cations are removed from soils by electrodialysis. Calcium was removed more easily and completely from the soils of the present investigation, than were any of the cations for which determinations were made. By subjecting a soil to a direct current of 110 volts with no resistance in the circuit, it was possible to extract by electrodialysis as much magnesium and potassium as was extracted with $N\text{ NH}_4\text{Cl}$. But during the process the temperature of the cell was such that it is probable that secondary reactions were responsible for the additional quantities of magnesium and potassium obtained. These cations may have come from certain soil minerals as well as from the colloidal fraction of the soil. It is generally assumed that only those cations which are present in the alumino-silicic and humic acids of a soil are capable of cationic exchange. In this event, the values for magnesium and potassium as obtained by means of the full-current dialysis are probably too high to be considered as including cations in exchangeable form only. If this suggestion is tenable, the question arises as to whether all of the magnesium and potassium recovered by means of $N\text{ NH}_4\text{Cl}$ from the soils under discussion are held exclusively in the colloidal complex, since the quantities so obtained are in close agreement with those liberated by electrodialysis when a current of 110 volts, without resistance, was employed. When a soil containing hydrogen, as a cation of its colloidal complex, is treated with $N\text{ NH}_4\text{Cl}$ the cation of the salt is absorbed and a portion of the hydrogen is expelled. This results in the formation of HCl , which may induce secondary reactions with the decomposition of the soil and a liberation of cations not a part of the alumino-silicic complex.

CATIONS EXTRACTED FROM ELECTRODIALYZED SOILS WITH NORMAL NH_4Cl

During the electrodialysis of a soil, hydrogen replaces the exchangeable cations which are expelled. In this way the colloidal fraction of the soil becomes more concentrated with respect to hydrogen and more acid in character. A soil with its absorbing complex more or less saturated with hydrogen as a result of electrodialysis, should, upon treatment with $N\text{ NH}_4\text{Cl}$, increase the acidity of the resulting solution more than would the same soil not previously electrodialyzed.

To determine the solvent effect of an acid so developed, two soils which had been previously electrodialyzed under the influence of a reduced current were treated and later leached with $N\text{ NH}_4\text{Cl}$. Before this was done, the electrodialyzed soils were freed of soluble anions by means of distilled water and

suction, after which they were removed from the alundum thimbles in which they had been dialyzed and air-dried.

The results of this test are shown in table 6. A comparison of the respective cations shown in this table can be made for the several methods used; electrodialysis, extraction with $N\text{ NH}_4\text{Cl}$ after electrodialysis, and extraction with $N\text{ NH}_4\text{Cl}$ without previous electrodialysis. The normal salt solution removed enough additional magnesium and potassium from the soils which had been previously dialyzed, to make the total quantities extracted from them agree closely with those removed by $N\text{ NH}_4\text{Cl}$ extraction alone. The quantities of magnesium and potassium removed from the soils by the salt solution after they had been electrodialyzed, as compared with the quantity of calcium so removed, are relatively large. The value shown for the removal of calcium by electrodialysis from the soil from Washington County is doubtless low. This is evi-

TABLE 6
Effect of electrodialysis on the quantity of cations extracted from soils with normal NH_4Cl

SOIL	METHOD	MILLIGRAM EQUIVALENTS PER 100 GM. OF AIR-DRY SOIL			
		Fe + Al	Ca	Mg	K
Vergennes clay, Jefferson Co.	Electrodialysis	0.76	10.97	2.42	1.02
	Extraction with $N\text{ NH}_4\text{Cl}$ after elec- trodialysis	4.82	1.25	6.07	1.26
	Total	5.58	12.22	8.49	2.28
	Extraction with $N\text{ NH}_4\text{Cl}$	0.65	10.93	9.30	2.18
Vergennes clay, Washington Co.	Electrodialysis	0.54	9.08	1.26	0.92
	Extraction with $N\text{ NH}_4\text{Cl}$ after elec- trodialysis	7.18	1.50	4.98	0.80
	Total	7.72	10.58	6.24	1.72
	Extraction with $N\text{ NH}_4\text{Cl}$	0.62	11.45	6.50	1.74

dent if the figure to which reference is made is compared with the corresponding figure of table 2 which is an average of several determinations. Hence, the total value shown for calcium should approach, more nearly, the value shown for this soil when it was leached with $N\text{ NH}_4\text{Cl}$ without being previously electrodialyzed. The quantities of iron and aluminum which were extracted from the electrodialyzed soils by $N\text{ NH}_4\text{Cl}$ deserve consideration. The quantities of these cations as extracted by electrodialysis and by leaching with $N\text{ NH}_4\text{Cl}$ do not differ greatly, but in comparison, the quantities obtained by leaching with the normal-salt solution after electrodialyzation are exceedingly large. It is likely that the iron and aluminum obtained, of which aluminum was more abundant, came from the decomposition of the alumino-silicate complex due to the acidity developed by the hydrogen which was absorbed by the soils during electrodialysis.

The results of the experiment with regard to iron and aluminum have some relation to the findings of Mattson (5). By treating soil-colloidal material

alternately with weak HCl and N NaCl, he found that iron and aluminum continued to be dissolved by the neutral-salt treatment as often as the soil material was rendered unsaturated by means of the acid.

It is likely that the cations extracted from acid soils with neutral-salt solutions, according to the procedure now in general use, often include cations which are not in true exchangeable form; the more acid the soil may be, the more likely is this condition to exist. The cations extracted by electrodialysis, with a suitable resistance in the circuit to provide an amperage of approximately 100 milliamperes, may approach more nearly the removal of those cations which are available for growing plants, than are the larger quantities obtained by means of a greater current or by means of N NH₄Cl. In any event, it is likely that the quantity of calcium extracted will be, within reasonable limits, approximately the same regardless of the method employed. But the quantity of other cations, particularly magnesium, will vary with conditions.

TOTAL EXCHANGEABLE CATIONS

It has been recommended by Bradfield (2) that the total quantity of exchangeable cations of a soil be determined by titrating the diffusates of electrodialyzed soils with suitable reagents. This is possible because the cations of the diffusates are present in the form of hydroxides.

The diffusates of the electrodialyzed soils of the present investigation were titrated for their total cationic content in the following manner. After any cations adhering to the surfaces of the cathode compartment were removed and added to the diffusates, an excess of 0.2 N H₂SO₄ was introduced. The diffusates were then concentrated on a steam bath to a volume of about 300 cc. During this process any carbon dioxide which may have been present was driven off. Excess H₂SO₄ was then ascertained by titration with 0.02 N NaOH using methyl red as an indicator. The total exchangeable cations determined in this way are shown in table 7. They are expressed in milligram equivalents of NaOH per 100 gm. of air-dry soil and are the averages of several determinations of close agreement. The first column of the table shows the sum of the three cations which were determined separately. It may be seen, by comparing the figures in the first two columns of the table, that the total exchangeable cations of the soils, as determined by titration, were made up principally of calcium, magnesium and potassium. This statement does not hold, however, for the soil listed second in the table, but this exception is a significant one. On the whole, the results imply that the quantity of exchangeable sodium in the soils is not large.

Electrodialysis was found to be a rapid and convenient means of estimating the total quantity of exchangeable cations in soil. It proved to be less complicated than the method based on the quantity of NH₄ absorbed from NH₄Cl. An attempt to measure cationic replacement in this way was unsuccessful. During the process of washing the excess NH₄Cl from the soils, which was often

extremely difficult, the soils in many instances became deflocculated and soluble organic matter appeared in the filtrates. Such a condition would necessarily vitiate any results obtained with the method.

HYDROGEN-ION CONCENTRATION BEFORE AND AFTER ELECTRODIALYSIS

The pH values of the soils of the investigation before electrodialysis appear in the third column of table 7. The soil which was most acid in character before electrodialysis, contained the smallest quantity of total exchangeable cations. But the relationship implied is not applicable to all of the soils. For instance, the Ontario loam soil from Oneida County of pH 7.4 contains a smaller

TABLE 7
Exchangeable cations in milligram equivalents per 100 gm. of air-dry soil
Hydrogen-ion concentration of soils before and after electrodialysis

SOIL	CATIONS Ca + Mg + K	TOTAL CATIONS IN TERMS OF NaOH	pH BEFORE DIALYSIS	pH AFTER DIALYSIS
Dutchess silt loam, Dutchess Co.....	6.53	7.48	5.2	4.2
Dutchess silt loam, Orange Co.....	3.10	6.73	4.3	4.0
Ontario loam, Monroe Co.....	12.42	12.13	7.2	4.3
Ontario loam, Oneida Co.....	12.26	12.63	7.4	4.6
Vergennes clay, Jefferson Co.....	14.25	14.24	5.7	3.9
Vergennes clay, Washington Co.....	12.15	12.10	5.4	4.1
Volusia silt loam, Allegany Co.....	8.18	8.88	4.8	4.2
Volusia silt loam, Cortland Co.....	7.34	8.60	5.0	4.1
Volusia silt loam, Tompkins Co. (Cayuta).....	10.24	11.39	4.9	3.8
Volusia silt loam, Tompkins Co. (Turkey Hill)	5.85	6.36	5.2	4.6
Dunkirk silty clay loam, Tompkins Co.....	6.20	7.00	5.7	4.3
Wooster gravelly silt loam, Cayuga Co.	4.57	5.70	4.8	4.4

quantity of exchangeable cations than does the Vergennes clay soil from Jefferson County of pH 5.7.

After the soils were subjected to electrodialysis for 8 hours, soluble anions were removed with distilled water by means of suction. The soils were then transferred from the alundum thimbles to small beakers, brought to air-dryness, and their pH values determined. These values are to be seen in the last column of table 7. They were found to approach, with some variation, a value of pH 4.0, which is higher than the value of pH 3.5 reported by Bradfield (1) for the soils with which he worked. Prolonged electrodialysis reduced the reaction values for those soils which were treated in this manner. The Vergennes clay soils from Washington and Jefferson Counties, after being electrodialyzed for 8 hours, were found to have reaction values of 3.9 and 4.1 respectively. Electrodialysis for 32 hours reduced each of these to pH 3.7.

SUMMARY

Twelve soils were studied with reference to certain exchangeable cations. These were determined by means of extraction with $N\text{ NH}_4\text{Cl}$ and by electrodialysis, and the quantities found were compared.

Soils of different types varied widely as to the quantity of the several cations extracted, as did, also, some of the soils of the same type. The quantity of cations present in the soils was, in some measure, an index to their fertility.

The quantity of calcium replaced by the two methods was in close agreement with a tendency for the electrodialytic method to give smaller values. But larger quantities of magnesium and, in some cases, larger quantities of potassium were extracted with $N\text{ NH}_4\text{Cl}$ than by electrodialysis under the influence of a direct current of suitable strength. The discrepancy between the methods was intensified when the exchangeable quantities of these latter cations were large.

When the soils were electrodialyzed with a direct current of 110 volts, with no resistance in the circuit, the electrodialytic and $N\text{ NH}_4\text{Cl}$ methods extracted about equal quantities of the three cations. This relationship together with the results obtained from fractional electrodialysis revealed the fact that calcium, which is the predominant replaceable cation in the soils of the investigation, is extracted more easily by electrodialysis than are magnesium and potassium.

Soils which had been electrodialyzed with a current of comparatively small amperage and freed subsequently of soluble anions, were leached with $N\text{ NH}_4\text{Cl}$ and the extractable cations determined. Relatively large quantities of magnesium, potassium, aluminum, and smaller quantities of iron, but comparatively little calcium were removed in this manner. The quantities of aluminum obtained signified a partial decomposition of the alumino-silicic complex.

Titrating the diffusates of electrodialyzed soils for total cationic content by means of standard solutions was found to be a rapid and convenient method for their determination. It proved more satisfactory than did the method based on the quantity of NH_4 absorbed from NH_4Cl .

The soils of the investigation, when electrodialyzed and freed of soluble anions, approached a reaction value of pH 4.0.

The results of the investigation suggest that the cations extracted from acid soils by means of $N\text{ NH}_4\text{Cl}$ may include certain cations which are not held in the absorbing complex of the soil, and hence, not exchangeable cations, as this term is usually employed. It is likely that the formation of HCl resulting from the absorption of NH_4 from NH_4Cl with the liberation of hydrogen, may partially decompose the colloidal fraction of the soil and certain of the soil minerals. It is possible that those cations which are extracted from soil by electrodialysis when the current-flow is relatively small represent, more nearly,

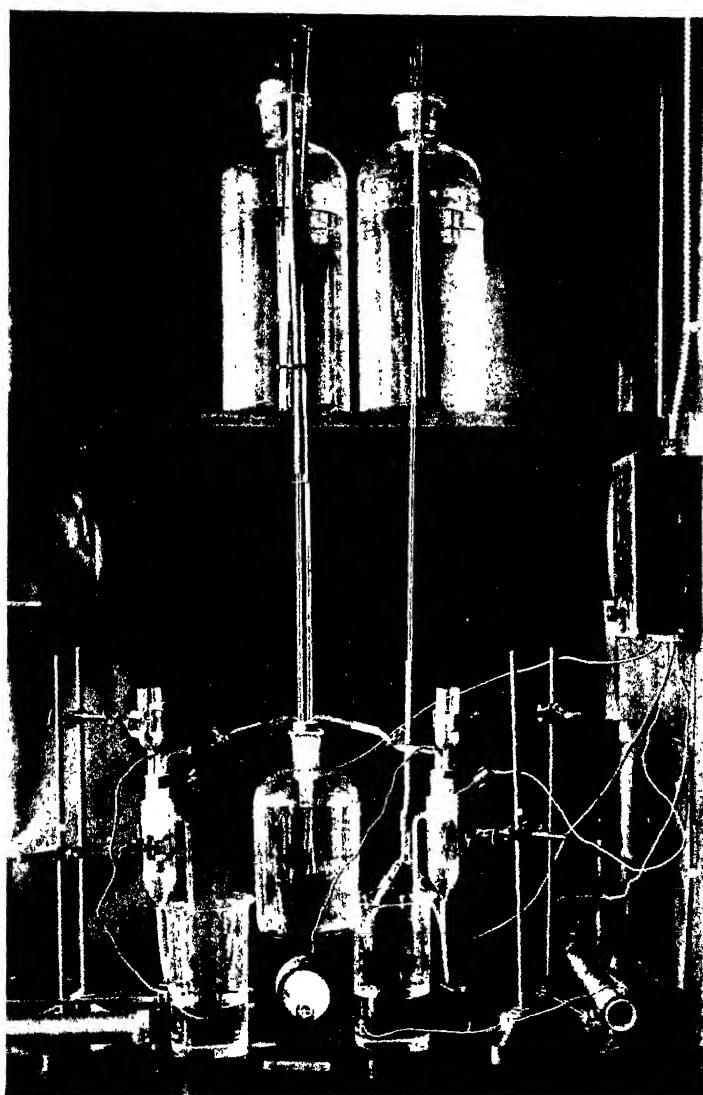
the cations which are available as nutrients for growing plants, than do those extracted with $N\text{ NH}_4\text{Cl}$.

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PLATE 1

THE APPARATUS USED FOR ELECTRODIALYSIS—SHOWN IN TWO UNITS



CROP RESPONSE TO LIME ON ACID SOILS

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Crops have been grouped according to resistance to acidity on the basis of both the quantitative and the intensity factors. The most modern grouping is according to acidity intensity, expressed as pH. In dealing with a soil by this measure it is possible either to select crops suited to the existing reaction or to change the reaction, by proper treatments, more nearly to meet the demands of any particular crop.

It is believed also that the presence of toxic ions, especially manganese and aluminum, is a very important detrimental factor in some acid soils. Accordingly tolerance for these ions has been given considerable attention, and crops have been found to vary in resistance to this toxic condition, which is an indirect result of the acid reaction of the soil.

Some considerable attention has been given to the nutrient needs of plants for calcium. Acid soils are fundamentally more deficient in this element, sometimes very much so, and certain plants, particularly the legumes, have been named as heavy lime feeders and therefore very sensitive to acid soil (4). Whether legumes are more sensitive to soil acidity directly or whether the effect is indirect through the legume organism may be open to question.

ESSENTIAL NUTRIENT CATIONS

The modern interpretation of soil acidity has resulted from the study of soil colloids. At the present time, from the soil standpoint, the burden of the problem of fertility is thrown upon the colloidal fraction. The amount, physical state, and chemical composition of the colloid practically determine the agricultural value of soils.

It is generally thought that the colloidal molecule or aggregate of the soil is a nearly insoluble acid molecule. A variable portion of the essential cations Ca, Mg, K, and the non-essential cations Na and H are tied to this molecule by loose chemical bonds not essentially different from the usual combinations. A certain portion of the cations which the molecule holds are the ions of exchange reaction. When calcium is exchanged for hydrogen, acidity results. When the exchange is for sodium, the final result is ruinous alkali. Calcium therefore becomes the dominant ion in the control of reaction, whether acid or alkali is considered.

Rather than total lime requirement, which has no standard measure, relative

TABLE 1
Upland soil samples, Astoria Branch Experiment Station lime requirement by horizons

PLOT NUMBER	TREATMENT	INCHES	CaCO ₃ (TONS PER ACRE)	EXCHANGE CALCIUM (LBS. PER ACRE Ca)	pH
1	Check	A 0-14	9.07	1,200	4.6
		B 14-30	5.10	400	5.0
		C 30-42	4.70	480	5.0
2	10 tons manure	A 0-14	7.45	1,680	5.1
		B 14-28	4.45	480	5.1
		C 28-41	4.21	280	5.1
3	2 tons lime, CaCO ₃	A 0-8	3.56	5,280	5.9
		B ₁ 8-20	5.26	1,360	5.8
		B ₂ 20-34	4.13	560	5.1
		C 34-42	3.48	560	5.1
4	2 tons lime, 10 tons manure	A 0-8	3.64	6,320	5.9
		B 8-24	5.18	720	5.1
		C 24-42	3.48	400	5.1
5	2 tons lime, 300 lbs. super	A 0-8	3.73	4,560	5.9
		B 8-28	3.97	560	5.4
		C 28-50	4.45	320	5.1
11	Check	A 0-8	7.86	720	5.2
		B ₁ 8-20	5.67	560	5.0
		B ₂ 20-28	3.64	320	5.1
		C 28-42	4.54	320	4.9
12	10 tons manure	A 0-8	8.42	1,680	4.8
		B 8-24	6.07	400	4.9
		C 24-42	4.13	320	5.1
13	200 lbs. NaNO ₃	A 0-12	7.69	1,360	5.1
		B 12-26	5.59	560	5.1
		C 26-42	4.78	360	4.9
15	300 lbs. super	A 0-8	6.56	1,280	4.8
		B ₁ 8-20	5.67	400	4.8
		B ₂ 20-26	4.86	280	5.0
		C 26-42	4.21	280	4.8
16	10 tons manure, 300 lbs. super	A 0-10	7.61	960	5.0
		B 10-30	6.16	480	5.0
		C 30-50	5.99	320	4.8
19	200 lbs. sulfur	A ₁ 0-8	5.99	960	5.0
		B ₁ 8-20	5.75	720	5.0
		B ₂ 20-28	3.73	320	5.1
		C 28-40	4.37	400	5.0

TABLE 1—Continued

PLOT NUMBER	TREATMENT	INCHES	CaCO ₃ (TONS PER ACRE)	EXCHANGE CALCIUM (LBS. PER ACRE Ca)	pH
20	200 lbs. sulfur, 10 tons manure	A 0-8 B ₁ 8-20 B ₂ 20-38 C 38-44	7.99 5.35 4.21 5.10	960 560 400 320	4.9 4.9 5.1 4.8
21	Check	A 0-8 B ₁ 8-24 B ₂ 24-30 C 30-42	7.69 5.26 3.48 5.35	960 560 240 400	14,000 13,200 8,400 9,200
22	10 ton manure	A 0-9 B ₁ 9-16 B ₂ 16-30 C 30-42	9.88 7.53 4.37 3.97	1,280 960 320 400	9,200 7,400 5,400 5,000
23	1000 lbs. rock phosphate	A 0-8 B ₁ 8-14 B ₂ 14-30 C 30-42	7.29 5.84 4.05 6.97	1,120 800 560 400	

amounts of exchangeable calcium and hydrogen may determine soil reaction and the need of lime. The greater portion of Willamette Valley and western Oregon soils are somewhat acid but only on relatively few is acidity developed to such an extent that lime is the dominant need. One such, a hill soil of moderately heavy texture, from the Astoria Branch Experiment Station shows a lime requirement by the Jones method (3) of 15,000 to 18,000 pounds per acre of CaCO₃ (table 1). On this soil, hydrogen equivalent to 23,000 pounds per acre of CaCO₃ can be easily replaced by calcium by leaching the soil with 2 per cent calcium acetate. Exchangeable calcium has been reduced to about 2,400 to 3,000 pounds per acre, all figures being reduced to carbonate equivalent. The easily exchangeable acidity is, therefore, approximately nine times the exchangeable calcium at the present time. Expressed in another way, the total calcium of the soil figured as carbonate is now only 35,000 pounds per acre, while easily exchangeable hydrogen is equivalent to two-thirds this amount, and exchangeable calcium to only 0.07 the amount. Crops respond readily to lime on this soil as shown by ten years of plot trials. The results of plot experiments show that lime has increased the yield of vetch from 1.55 tons to 2.70 tons per acre, almost doubling the yield. Vetch can not be grown successfully without lime or manure. With three years' results on red clover, the increase in yield was nearly one-half ton per acre. Where lime or manure is

not used, clover disappears and weeds come very quickly. According to A. E. Engbretson, in charge of the Astoria Branch Experiment Station (1), lime is the outstanding need on this and similar soils of the locality, although manure to some extent takes the place of lime.

A study of the hydrogen-ion concentrations shows that the untreated soil varies from pH 5.2 in the surface, with a tendency for the parent material to run a little less acid. The use of limestone has brought the pH in the surface soil to 5.9. The effect of the lime in reducing acidity has not extended in most

TABLE 2
Rotation plots—Range C, Willamette silty clay loam

TREATMENT	PLOT	REPLACEABLE CALCIUM (POUNDS PER ACRE)	pH	COMBER TEST	REPLACEABLE HYDROGEN EQUIV. CaCO ₃ , TOTAL POUNDS PER ACRE
3 tons CaCO ₃	17a	6,960	6.6	Very slight	3,520
	17b	5,040	6.4	Medium	3,520
	17c	8,160	6.5	Medium	
Check.....	18a	5,840	6.1	Strong	5,680
	18b	4,880	6.3	Medium	3,520
	18c	8,640	6.7	Medium	
6 tons CaCO ₃	19a	9,600	7.2	None	2,880
	19b	5,360	6.3	Slight	4,200
	19c	9,280	6.8	Strong	
9 tons CaCO ₃	20a	11,660	7.7	None	920
	20b	5,680	6.8	Slight	
	20c	8,480	6.7	Strong	
Check.....	21a	6,960	6.5	Medium	4,320
	21b	5,520	6.2	Medium	
	21c	8,000	6.6	Medium	
12 tons CaCO ₃	22a	12,000	7.3	None	1,160
	22b	5,120	6.3	Medium	
	22c	8,480	6.6	Strong	

Note: Calcium replaced with 0.05*N* HCl. Hydrogen replaced with 0.1*N* calcium acetate.

cases much into the subsoil. The acidities correlate very well with the exchangeable calcium. It is apparent that the soil is inherently deficient in calcium, as shown by the low exchangeable calcium and the high acidity of the parent soil-forming material.

The cause for the high acidity developed along the coast in the Astoria region may be credited in part to climatic conditions. The annual rainfall at Astoria, averaged for 64 years, is 76.99 inches. Such heavy rainfall is accompanied with heavy leaching of calcium. The soil also, though heavy in

texture, has a porous crumb structure which allows most of the water to pass through and little to pass off the surface. Whether porous soil structure is a cause or a result of the heavy leaching cannot be stated. The hill soils appear to show a structure similar to southern lateritic formations. These soils do not become water-logged, and the structure is, therefore, very favorable to crop production.

A contrast to the above condition is found in certain soils of the Willamette Valley. One of the best soils, which belongs to the Willamette series, runs consistently low in both acidity and lime requirement and the response to lime is slight. Samples from check plots on the Oregon Agricultural Experiment Station at Corvallis show this soil to run 14,600 to 17,400 pounds per acre of exchange calcium calculated as CaCO_3 (table 2). The exchange hydrogen amounts to only 4,300 to 5,600 pounds in calcium carbonate equivalent. In this case the acidity is only about one-third the exchange calcium calculated in equivalents, the reaction is around pH 6.0 to 6.5, and the crops show only slight response to lime. This and similar data available indicate that when the supply of exchangeable calcium is greater than the exchangeable hydrogen equivalent, the soil is not likely to show much response to applications of lime. When, however, exchangeable calcium is low and the exchangeable hydrogen equivalent high, lime is very likely the dominant need of the soil.

The above data are for the surface horizon of the soil, and the amounts are calculated for the cultivated depth of $6\frac{2}{3}$ inches. The condition of the subsoil and the parent soil-forming material may also have some significance. Even on the most acid cultivated soils that have not been limed, the supply of exchange calcium may be greater in the surface than in the deeper layers. The check plot on the Astoria soil described in the foregoing, showed 2,400 pounds per acre of exchange calcium in carbonate equivalent in the surface horizon. In the B_1 horizon there was 1,400 pounds, in the B_2 horizon only 600 pounds, and in the parent material 1,000 pounds per acre. The lime requirement varied also in the same way instead of inversely. In the corresponding horizons the lime requirement was 16,000 pounds, 10,600 pounds, 7,000 pounds, and 10,800 pounds, respectively. But the surface soil also shows the highest exchangeable hydrogen, 23,000; 18,600; 13,400 and 12,600 pounds, respectively downward (see table 1). Thus the lime requirement, exchangeable calcium, and exchangeable hydrogen are all much higher in the surface soil. Data are not available to explain this condition. Perhaps it is due to the humus which is present in the surface soil. Peat soils in which humus is very abundant show higher buffer action than mineral soils, which would indicate that humus of ordinary soils might hold a large amount of exchangeable calcium and at the same time show a large amount of exchangeable hydrogen.

The condition of reduced amount of exchangeable calcium in the subsoil might be explained if calcium in cultivated soils moves in two directions, both up and down. Downward movement due to leaching results ultimately in complete loss. Upward movement due mainly to the action of plants in

gathering this nutrient in relatively large quantities, causes accumulation in the surface, especially where much crop residues are returned to the land. Such movements, however, do not account for the greater amount of exchangeable hydrogen in the surface horizon.

The reduced amount of exchangeable calcium in the subsoil may account for the condition noted in some acid soils, that plant roots are dwarfed, stunted, and stubby, and fail to penetrate to any great depth. The injury of the toxic ions of acid soils should be greater in the subsoil because of the above condition. Relatively light surface applications of lime, however, are usually adequate to correct the condition. Since lime does not move very rapidly into the deeper soil the increased supply of soluble calcium, even though it is limited to the surface soil is sufficient for correcting the acid condition as far as the plant is concerned. However, limestone must be applied several months ahead of the crop and thoroughly worked into and mixed with the surface soil where the feeding roots of the plant are able to obtain it, if best results are to follow.

A very interesting result is obtained from the study of culture solutions. Most crops appear to thrive with rather high acidity if essential nutrients are supplied in sufficient abundance. This result indicates that acidity may not be of direct serious injury to many crops and that available calcium or other essential nutrients may be a large factor in the acidity problem. Since few humid soils contain calcium in the form of carbonate, the exchangeable form must be the chief source available to plants. Low exchangeable calcium and high exchangeable hydrogen, therefore, are decidedly unfavorable to crops from the calcium standpoint.

In acid soils, calcium is nearly always the only cation other than hydrogen that is given consideration, though magnesium functions in a similar exchange reaction. Total analyses of some of the Willamette Valley soils show only traces of magnesium, and others are low. The best soils run as high as 30,000 pounds per acre of magnesium figured as carbonate. Exchangeable magnesium necessarily runs low or is present only in traces on those soils which contain little total magnesium. Since lime corrects acidity, magnesium may be overlooked. Lack of magnesium, however, is probably more an inherent deficiency than result of the development of an acid condition. Since plants need magnesium, the use of magnesium lime on some soils especially deficient in this element might prove beneficial. Some such soils are under study at the present time.

There is little or no established relation between the reaction of the soil and the amount of available potassium. On some soils the correction of acidity by the use of lime increases the amount of available potassium, presumably by exchange reaction, but this is not always true. Most agricultural soils are well supplied with potassium, in spite of heavy leaching which may have produced considerable acidity, and good farming practice to maintain general fertility usually maintains a soil in a satisfactory state to supply adequate available potassium.

ESSENTIAL ANIONS IN ACID SOILS

In order to combine chemically with the cations, the complex colloidal alumino-silicate aggregate must function as an anion. The cations so held are not very soluble and are thus prevented from leaching. But weak acids, especially carbonic, gradually bring them into solution. They are thus conserved and yet are available to crops.

Anions, especially the phosphate ion, may prove to be similarly held. To hold the anions by chemical combination the colloidal complex aggregate must function as a cation. The important anions are sulfate, nitrate, and phosphate. Of these the nitrate ion is so loosely held that water extracts it almost completely. This ion, therefore, probably does not combine with the colloidal soil complex. The phosphate ion, on the other hand, is held very tenaciously by soils. The higher the colloidal content of the soil, the greater the apparent ability of the soil to absorb and hold phosphate.

As evidence that cations other than a colloidal ion hold phosphate, it has been found that soils long leached of calcium have also lost appreciable amounts of phosphate (5). This would indicate that calcium is a very important cation which enables soil to take up phosphate. Soils which have been electrodialyzed or leached with acid to remove all their exchangeable bases lose some but not all of their capacity to absorb phosphate. Roszmann (6) found that the electrodialyzed soil would take up most phosphate at pH 3 to 4. He believes that the organic matter of the soil may function as a cation to take up phosphate. No doubt, however, much of the phosphate in ordinary soils is in the form of colloidal, precipitated, tricalcium phosphate. A considerable portion of phosphate may be held sometimes in the organic form, as an essential part of the protein molecule.

Willamette Valley soils, regardless of degree of acidity, show very little water-soluble phosphate, in most cases less than one part per million. Phosphate is undoubtedly a limiting factor on many acid soils. Root crops on the very acid Astoria soil respond readily to phosphate treatment whereas clover does not, indicating that the crop as well as the soil is an important factor.

Application of limestone to acid soils some time before phosphate is used seems advisable, although either acid or neutral soils show great power to take up soluble phosphate. Texture as well as reaction is an important factor in determining ability of the soil to absorb phosphates. Applications of soluble phosphates on medium to heavy valley soils at field rates of 250 to 500 pounds per acre fail to result in any appreciable amount of water-soluble phosphate in the soil (table 3). Very commonly such an application does not produce sufficient soluble phosphate to respond to a sensitive color test. On light textured soils, however, the effect is reversed, and the soil is unable to absorb either physically or chemically any very large quantities of phosphate.

Though regardless of reaction, heavy textured soils absorb and hold large amounts of phosphate, crops grown on such soils usually show ready response

	<i>Third sampling</i>									
	0.0100	0.0011	0.0021	0.0000	5.6	5.1	Strong	0.020	59	6
1. Check.....	0.0111	0.0021	0.0045	0.0000	6.4	5.6	Slight	0.014	95	7
2. CaCO ₃ , 1 ton.....	0.0111	0.0021	0.0045	0.0000	6.9	6.3	None	0.011	167	5
3. CaCO ₃ , 2 tons.....	0.0187	0.0065	0.0057	0.0019	7.6	7.6	None	0.100	250	20
4. CaCO ₃ , 4 tons.....	0.0267	0.0192	0.0046	0.0032	6.6	6.2	Slight	0.022	100	6
5. CaCO ₃ , 1 ton; AP, 250 lbs.....	0.0128	0.0053	0.0057	0.0018	6.9	6.7	None	0.022	167	4
6. CaCO ₃ , 2 tons; AP, 250 lbs.....	0.0256	0.0071	0.0079	0.0049	6.4	6.0	Slight	0.022	90	4
7. CaCO ₃ , 1 ton; AP, 500 lbs.....	0.0079	0.0038	0.0065	0.0021	6.9	6.4	None	0.024	167	7
8. CaCO ₃ , 2 tons; AP, 500 lbs.....	0.0225	0.0101	0.0123	0.0060	6.9	6.4	None	0.033	167	13
9. CaCO ₃ , 2 tons; manure, 10 tons; AP, 500 lbs.....	0.0261	0.0138	0.0119	0.0079	6.9	6.5	None	0.033	167	13

to phosphate treatment. The most acid soils of the Willamette Valley respond readily to phosphate as well as lime with most crops grown. Since commercial phosphates usually contain large amounts of soluble calcium it is possible that not always is all the crop response due to the phosphate ion, even where lime is not used. The red hill soils of the valley, which are usually acid, show marked response to phosphate treatment, however. A soluble phosphate, such as super, is much more effective than rock phosphate.

On poor acid mineral soils, nitrogen deficiency is usually quite marked. Since the major portion of the nitrogen of the soil is in organic combination, whatever limits the growth of plants, in the long run limits the supply of nitrogen. Acidity, therefore, limits the nitrogen supply and also the rate at which nitrate is liberated. Organic matter has marked effects on the soil reaction. As cations neutralize acidity so anions increase it. When nitrate is produced in the soil an equivalent of anions, mostly calcium, must combine with it. Large amounts of nitrate are lost by leaching, and when 100 pounds of nitrate is thus lost about one-third that much calcium is taken with it. Lysimeter studies at Oregon (2) show annual losses of nitrate at the rate of 26 to 35 pounds per acre on untreated soils.

The loss of the calcium equivalent is not large but is persistent. By far the greater loss of calcium, however, is in the form of bicarbonate, and it is generally thought that the ultimate effect of adding organic matter to soils is to save rather than to increase the loss of lime, because of the formation of insoluble lime humate.

Since acid soils are very often low in available nitrate, a desired effect of a lime application is to increase nitrate. This does not necessarily occur, however (7). Lime increases the number and activity of soil organisms but does not always increase nitrification unless fresh nitrifiable material is added to the soil. When ammonium sulfate or nitrogen-rich organic materials are added, a marked increase in nitrification occurs because of the addition of lime (table 3). In fact, lime may increase nitrification when soils are not acid if nitrifiable material is added also. Many failures of crops to respond to lime, and especially failure of non-legumes to respond to lime, are in all probability due to the fact that lack of nitrate as well as the presence of acidity is a limiting factor in crop production. This perhaps is equivalent to stating that the general fertility of acid soils must be built up to insure crop response to lime applications. On the poorer Willamette Valley soils lime shows much better results when supplemented with a source of nitrogen.

The other important anion, the sulfate ion, is perhaps not closely related to soil reaction. It appears from data available, however, that sulfate in solution is largely in combination with calcium (table 3). The limited supply of calcium in acid soils, therefore, should limit the supply of soluble sulfate. A large portion of the reserve of sulfur in soils is no doubt in organic combination. Correction of acidity by the use of lime produces a decided stimulation to the breaking down of organic matter and may thus liberate sulfate as CaSO_4 .

which passes into solution. Since acid soils are likely to be low in organic matter and, therefore, low in organic sulfur, the effect of lime applications to increase available sulfate would appear to be somewhat limited.

In the Willamette Valley, acid soils very often respond to gypsum treatments in growing legumes. Such response could be due to either the sulfate or the calcium ion, or even to an indirect effect. Even sulfur which quickly increases acidity, may stimulate legumes on acid soils. As lime increases the amount of available sulfate, so does an application of sulfur increase available calcium (8, 9), and again it is not possible to relate the crop response directly to the sulfate ion.

CONCLUSION

The situation may be summed up by stating that fertility is expressed in the ability of a soil to produce a crop, and the crop yield therefore is a measure of fertility. Whatever maintains general fertility, which means all those factors present in the soil that determine crop producing power, maintains the most valuable agricultural soil. Plants require both cations which are acid neutralizers, and anions which are functionally acid. The two groups of ions are in the soil partly in combination with each other and, to a much larger extent, in combination with a nutrient, non-essential but materially necessary, colloidal complex both mineral and organic. This acid complex holds the reserve supply of essential nutrients, the ability of which to supply the growing crops is very decidedly affected by the reaction. The reaction of the complex, depends in turn upon the relative supply of essential cations and anions and especially upon the ratio of the essential reaction regulating cation calcium and the acid cation hydrogen. It seems probable that the supply of available essential ions, rather than the degree of acidity or even the concentration of toxic ions, is the greater factor in crop production. This fact is recognized in the statement that fertile soils, though acid, may not be greatly in need of lime. It is recognized also in certain lime requirement methods which are graduated to a theoretical scale of fertility. The poorest soils are given the heaviest application of lime whereas for the best soils is recommended a much lighter application. In Oregon it is most common to recommend not less than one ton of lime per acre, which is the practical minimum limit, and not more than two tons, which is the economic maximum limit. Rather than use heavier lime applications, it is recommended to build up and maintain general fertility. When all is stated, however, no factor or group of factors entirely control fertility. Physical soil conditions or climatic factors may at times overshadow all others. The conclusion must be, therefore, that there are several factors of fertility and great care is essential in diagnosing poor acid or infertile soils by the use of laboratory methods.

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RETENTION OF PHOSPHATE BY HYDRATED ALUMINA AND ITS BEARING ON PHOSPHATE IN THE SOIL SOLUTION

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The retention of phosphate by the soil and the mechanism by which this effect is obtained have been repeatedly discussed in journal articles. Recently the work of Teakle (4) and of Roszmann (3) have thrown added light upon the subject. Teakle finds that the phosphates of aluminum, iron, and manganese are least soluble under slightly acid conditions. At higher pH values phosphate is liberated. Rozsmann, in studying phosphorous adsorption by electrodialyzed colloidal clay, found a maximum adsorption at pH values of from 3 to 4. The concensus of information indicates that phosphate is bound by colloids of the type found in soils when the environing solution is slightly acid. Under neutral or alkaline conditions some or all of the phosphate is liberated.

PURPOSE OF THE INVESTIGATION

In connection with certain researches upon a related subject it was necessary to study the composition of the solid phase formed when alumina is precipitated in the presence of phosphate ion. Since the results have an immediate bearing upon the question of the retention of phosphate by soil colloids, they are here set forth.

METHODS AND RESULTS

As a preliminary step in this research an electometric titration of a solution, such as it was intended to study, was first made. In this case 0.01 *M* AlCl_3 solution containing an equivalent quantity of KH_2PO_4 was titrated by NaOH at 30°C. The pH value after each small increment of NaOH, was determined by means of a hydrogen electrode and the auxiliary equipment necessary for precision measurement. The solutions used throughout this research were carefully made up from purified reagents and distilled water. The results are plotted in figure 1. The curve obtained suggests that the aluminum hydroxide upon precipitation carries down with it an appreciable quantity of the negative radicals present and that these are partially or completely released at higher pH values [In this regard cf. Theriault and Clark (5) and Miller (1)].

In order to determine the extent to which the phosphate ion was carried down by the precipitating alumina at different hydrogen-ion concentrations, the following experiments were conducted. Five hundred cubic centimeter por-

tions of a 0.02 *M* solution of AlCl_3 containing an equivalent quantity of KH_2PO_4 were precipitated in each case by the slow addition of 500 cc. of a solution containing NaOH, the concentration of the alkali being varied in each experiment. The pH of the solution, after the precipitate was allowed to settle, was determined colorimetrically. The precipitate was first washed with distilled water by decantation, then brought upon a hardened filter paper and washed as completely as possible with a large quantity of water, always keeping the precipitate flooded and as thoroughly stirred as possible. The

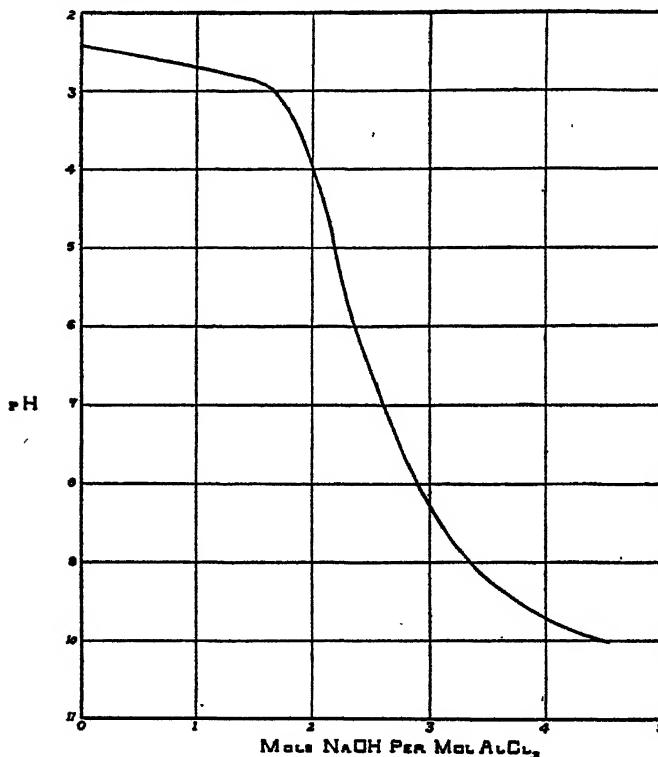


FIG. 1. ELECTROMETRIC TITRATION OF $\text{AlCl}_3-\text{KH}_2\text{PO}_4$ SOLUTION

precipitates proved very refractory to handle because of their strong tendency to form stable colloidal dispersions during prolonged washing and thus be lost. It is, therefore, probable that small amounts of soluble phosphate adhered to the precipitate because of incomplete washing, rendering the analytical results slightly too high in phosphate. The precipitate was finally dried and analyzed for Al_2O_3 and P_2O_5 . The results are plotted in figure 2. The conclusions to be drawn are as follows:

1. From the pH value at which precipitation begins up to a pH value of 4.5 the mol ratio of Al_2O_3 to P_2O_5 is 1:1; that is, the precipitate has the composition AlPO_4 .

2. At higher pH values the phosphate content of the precipitate rapidly decreases. The hydrogen-ion concentration at which the phosphate content of the precipitate becomes zero was not realized since the precipitates formed at the higher pH values are extremely colloidal and difficult to study. The indications are, however, that at pH values above 8.5 the phosphate content of the solid phase becomes small.

A qualitative determination of the range of hydrogen-ion concentration over which precipitation is most complete was also made. It is difficult or impossible to determine this value with exactness, except according to some arbitrary standard, for the following reason. In most of the experiments some of the solid phase formed a gelatinous precipitate while a part remained in colloidal

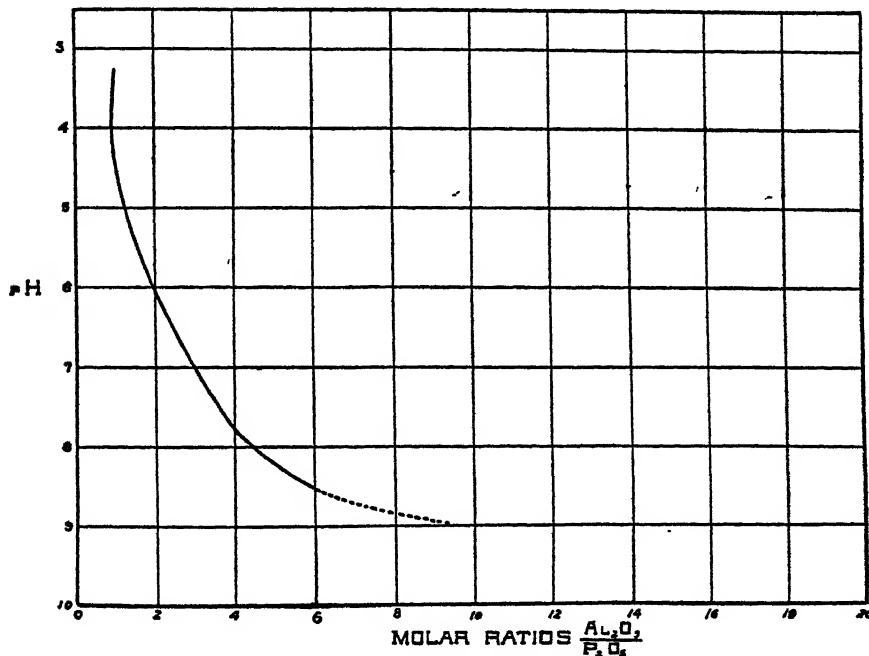


FIG. 2. COMPOSITION OF PRECIPITATE

dispersion. A little vigorous stirring caused a larger portion of the precipitate to disperse more or less permanently. Upon filtering, a greater or less quantity of the solid phase was retained, depending upon the type of filter used. Even a very dense, hardened filter, however, failed to remove all of the dispersed material.

The results, although qualitative, indicate definitely that the range of least solubility for the alumina lies between the pH values of about 4.5 to 7.5. In solutions more acid than pH 4.5 the alumina dissolves to form aluminum salts. At pH values above 7.5 soluble aluminates are formed, solution of the solid phase being more complete at higher pH values.

DISCUSSION

The results of this investigation indicate the effect of hydrogen-ion concentration upon the capacity of a hydrated alumina precipitate to retain phosphate. The mechanism of the process as deduced from the experiments here and from a comparison with similar systems (1) appears to be as follows:

1. The specific capacity of the hydrated precipitate to retain phosphate is greatest from the hydrogen-ion concentration at which precipitation begins (in this case from a pH value of about 3) to the hydrogen-ion concentration at which the precipitation of alumina is complete (pH value of about 4.5). The precipitate over this range of hydrogen-ion concentration has the composition AlPO_4 .

2. From the point at which precipitation is practically complete (pH value of 4.5) further addition of alkali causes a change in the composition of the solid phase during which the phosphate group is progressively replaced by hydroxyl, the phosphate going into solution. This continues until all the phosphate is replaced.

3. Before the replacement of phosphate by hydroxyl in the solid phase is complete, however, a further chemical reaction begins. Above a pH of about 7.5 the precipitated alumina begins dissolving, because of the formation of soluble aluminates.

4. Between pH values of approximately 7.5 to 8.5 the reactions described in 2 and 3 proceed simultaneously. Above a pH value of 8.5 the phosphate content of the precipitate is negligible. Further addition of alkali causes the remaining precipitated alumina to form soluble aluminates.

If it is permissible to apply the results of this work upon hydrated alumina to the hydrated alumina contained in soil colloids (and no doubt it is permissible to do so to a limited extent) we obtain some notion of the mechanism by which this substance retains phosphate in the soil under slightly acid conditions and liberates it when the soil solution is rendered more alkaline.

The mechanism by means of which hydrated ferric oxide retains phosphate is similar to that for hydrated aluminum oxide. In the case of iron, precipitation begins at a somewhat lower pH value than for alumina in solutions of the same concentration. The situation is simplified by the fact that compounds similar to the soluble aluminates are not formed; and complicated by the possibility of reduction to the ferrous state (at least in the soil).

It must be emphasized, however, that the particular results obtained in this research apply strictly only to the particular system here described. Care and judgment must be exercised in the application of the conclusions to apparently similar systems, such as the soil solution. For example, with changed concentrations of solution, the range of hydrogen-ion concentration over which precipitation of alumina is practically complete will broaden or narrow accordingly as the concentration is increased or decreased. With the introduction of other ions, especially anions, the system changes greatly in its reactions (2). If these facts are borne in mind, the conclusions derived here are of general application.

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THE EFFECT OF DIFFERENT PROPORTIONS OF CALCIUM
NITRATE AND POTASSIUM DI-HYDROGEN PHOSPHATE
ON THE GROWTH OF WHEAT IN SAND CULTURES¹

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The fertilizer problem of the Middle West involves, in general, the use of nitrogen and phosphorus. An experiment by Sewell (11) has shown that the supply of nitrogen during the fruiting phase of growth will influence the plant's response to phosphorus. The purpose of the study here reported was to observe the effect of three different proportions of calcium nitrate and potassium di-hydrogen phosphate during the seedling, vegetative, and fruiting stages of growth.

EXPERIMENTAL METHODS

Marquis wheat was grown in sand cultures, five plants to each container, according to a plan presented by a special committee of the division of biology and agriculture of the National Research Council (8).

The experiment was started September 24, 1924, and the plants were harvested April 17, 1925; a period of 206 days. Each treatment was arranged in a series of 10 cultures, which are hereafter designated as series I, II, and III. The solutions were selected from type 1.

SERIES NUMBER	SOLUTION NUMBER	MOLECULAR PROPORTIONS		
		KH ₂ PO ₄	Ca(NO ₃) ₂	MgSO ₄
I	1R1S4	1	4	3
II	1R2S3	2	3	3
III	1R4S1	4	1	3

Ferric phosphate was added occasionally to supply iron.

At the end of each 3½ days, reaction changes were measured by pH readings, using the indicator method proposed by Wherry (15). An attempt was made in each case to bring the reaction back to that shown by fresh solution in contact with sand. This was shown to be as follows:

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SOLUTION	REACTION
R1S4	7.0
R2S3	6.5
R4S1	5.5

Reactions in each case tended toward neutral during the absorption period as established by Prince, Jones, and Shive (10).

Temperature and evaporation were recorded, the latter by the white porous cup atmometers as suggested by Livingston (7). The weekly mean temperatures varied from 51 to 75°F. The lowest weekly minimum was 38 and the highest 69°. The lowest weekly mean maximum was 62 and the highest 89°. The highest temperature recorded for any day was 92°. The average daily evaporation as determined by two atmometers was 14.56 gm. The maximum for a 3½-day period was 90 gm. and the lowest 17.5 gm.

TABLE 1
The relation of cultural solutions to several growth factors in wheat
Average of 7 cultures

SERIES	TILLERS PER PLANT	TRANSPIRATION PER CULTURE				HEIGHT OF PLANTS ON JAN. 5	DATE OF HEADING
		Seedling stage	Vegetative stage	Fruiting stage	Total		
I	6.0±1.8	1663±13.9	12764±958	15174±127	29766±103	15.8±0.27	Mar. 4
II	5.8±0.2	1735±14.4	9659±465	8717±404	19545±1174	16.2±0.53	Feb. 13
III	4.5±0.1	1308±21.6	8629±146	10857±143	20598±315.2	14.1±0.13	Feb. 6
NUMBER OF DISEASED HEADS		NUMBER OF CULMS AT HARVEST PER CULTURE	NUMBER OF HEADS AT HARVEST PER CULTURE	NUMBER OF STERILE HEADS PER CULTURE	DRY WEIGHT OF TOPS	DRY WEIGHT OF ROOTS	WEIGHT OF GRAIN
I	2.5±0.36	51±0.90	18±1.20	12±0.86	81.4±1.08	9.1±0.19	0.66
II	6.5±0.30	36±1.31	7±0.12	5±0.84	49.3±3.20	4.5±0.29	0.49
III	2.7±0.23	30±0.12	7±0.76	5±0.52	48.6±1.24	12.4±0.21	0.95

RESULTS .

The most marked visual effect on growth was the increased tillering and heavy succulent growth in series I, containing the high proportion of nitrogen. Series II showed a similar effect as compared with series III. Series III was characterized throughout the experiment by a stiff, slender, sparse-leaved growth. Data relating to tillering, transpiration, height of plants, dates of heading, number of culms and heads, and weights are presented in table 1.

The plants in series II became chlorotic after the seedling stage and showed injury and growth abnormalities. Leaves coming out of the boot were curled.

The plants in series I did not show injury but were subject to attacks of mildew and aphids, due perhaps to tender, succulent leaves and stems. The time of heading was irregular, and the grain production did not seem to be normal. Some of the plants were infected with *Helminthosporium sativum*.

In order to determine whether the abnormal growth was due to the small volumes of sand used, three cultures from each series were transferred to 4-gallon jars of sand on March 28. These plants were disregarded at harvest and only the observable effects of the changes noted. The transplanted cultures were fed solution or watered in the bottom of the jar. The transferred cultures were:

<i>Series I</i>	<i>Series II</i>	<i>Series III</i>
Culture no. 6	Culture no. 11	Culture no. 23
Culture no. 9	Culture no. 12	Culture no. 26
Culture no. 10	Culture no. 20	Culture no. 28

Series I showed no response, series II showed some renewal of growth, but the plants in series III responded markedly. Some of the very small culms grew up and headed in a short time. The roots in series III were solidly matted and showed a characteristic "pot-bound" appearance. Hoagland and Martin (5) suggest that solution volume may be a limiting factor in sand culture work under the present methods, and there are indications, both from the amount of solution supplied and the cramped root space, that this is true with respect to series III.

The probable error of the mean was calculated according to Bessel's formula; $Em = 0.6745 \sqrt{\frac{d^2}{n(n - 1)}}$, and the probable error of the experiment was considered as the arithmetical average of the errors of the mean. This, in the case of the dry weights of tops, is 1.84. The probable error of a difference is $1.84\sqrt{2} (= 2.59)$ and hence a statistically significant difference must be at least 8.29 (i.e. 3.2×2.59). It can be seen readily that the difference between the dry weights of tops in series II and III is not statistically significant, whereas the differences between series I and II and between series I and III are highly significant.

In comparing weights of roots the probable error of the experiment was found to be 0.23 and the probable error of a difference, 0.32. A difference, to be significant, should be 0.32×3.2 or 1.02 gm. Series I produced a significantly higher yield than series II, and series III was significantly higher in yield of roots than either series I or II.

Series III matured the most grain, but differences with respect to grain yield should not be emphasized on account of abnormalities of growth in each series, previously mentioned.

CHEMICAL DETERMINATIONS

After harvest the aerial parts of the plants were composited for an analysis of the inorganic ash constituents. The methods suggested by the Association

of Official Agricultural Chemists (1), with the exception noted below³ were followed.

The procedure by Latshaw (6) was used to oxidize the sample for the determination of sulfur and phosphorus. After ashing very carefully in order not to volatilize the chlorides, and after dehydrating the silica, the calcium and magnesium were determined by the McCradden method (9). Organic compounds in the magnesium filtrate were oxidized by evaporating the filtrate to dryness with strong nitric acid before determining iron and aluminum.

Discussion of data on chemical analysis

The chemical data are presented in tables 2 and 3. The percentage of phosphorus, potassium, and calcium vary with the amounts of these elements

TABLE 2
Ash constituents of wheat plants based on percentage of dry matter

SERIES NUMBER	SAMPLE NUMBER	N	TOTAL ASH	SAND AND SILICA	P	K	Ca	Mg	S	Fe	Al
1	1	2.13	8.29	0.86	0.361	1.02	1.03	0.73	0.77	0.057	0.064
1	2	2.14	8.40	0.93	0.357	0.94	1.00	0.71	0.76	0.061	0.092
2	3	2.25	11.00	1.76	0.530	2.42	0.64	0.72	0.91	0.050	0.076
2	4	2.28	10.99	1.62	0.531	2.34	0.68	0.67	0.93	0.044	0.072
3	5	1.24	9.95	0.68	1.126	3.00	0.26	0.31	0.75	0.044	0.088
3	6	1.26	10.05	0.69	1.121	3.17	0.27	0.31	0.75	0.048	0.100

TABLE 3
Ash constituents of wheat plants based on percentage of dry matter

SERIES NUMBER	N	TOTAL ASH	SAND AND SILICA	P	K	Ca	Mg	S	Fe	Al
I	2.13	8.34	0.89	0.359	0.97	1.01	0.72	0.76	0.059	0.078
II	2.26	11.00	1.69	0.530	2.38	0.66	0.69	0.92	0.047	0.074
III	1.25	10.00	0.68	1.123	3.08	0.26	0.31	0.75	0.046	0.094

in the culture solution. Most of the Ca, Mg, K, and PO₄ was observed to be in water-soluble form. Waynick (14) has shown that the ash constituents of plants grown in different solutions vary widely. Hoagland (3) has found increased percentages of N, K, Ca, and PO₄ in barley plants, with the increase of these elements in culture solutions.

Nitrogen is much lower in series III than in I or II. This variation is in accord with the amount in the culture solutions. The percentage of nitrogen is higher in series II than in series I, whereas the opposite is true of the culture solution. Perhaps, as Hoagland (4) found, the high percentage of calcium in

³ Chemical analyses were made under the direction of W. L. Latshaw, chemistry department.

the culture solution of series I has inhibited the absorption of the NO_3^- ion. Also the high permeability of the plants in series II, shown by their high total ash, might be the cause of the greater absorption of NO_3^- .

Magnesium decreased with the increase in potassium. The increased absorption of potassium in series II and III was accompanied by an increase in total ash. Apparently the increased absorption of potassium depressed the absorption of magnesium. True (13) has shown that potassium will replace the calcium and magnesium in the pectates of the middle lamella, causing the cell wall to become more permeable. The percentages of sulfur, iron, and aluminum did not vary widely.

Total ash and ash constituents seem very high throughout the experiment (2). Snyder (12) gives the ash of wheat straw as 5.37 per cent. In this experiment the total ash varied from 8.34 to 11.00 per cent.

SUMMARY AND CONCLUSIONS

Marquis wheat was grown to maturity, over a 206-day period, in sand cultures of three series, 10 jars to a series. The effect of different osmotic proportions of nitrogen to phosphorus potassium salts was tested, the three solutions having a constant proportion of MgSO_4 . All solutions had a total concentration of one atmosphere.

Solution 1R1S4 with the high proportion of calcium nitrate produced the most tillers, the greatest dry weights of tops, and the greatest total transpiration. Tillering seems to be in proportion to the nitrogen in solution. Series I and II were characterized by a heavy, succulent growth. Series III, with a high proportion of potassium di-hydrogen phosphate, was characterized by fewer tillers and a slender, sparse-leaved growth.

During the vegetative phase, chlorosis appeared in series II, accompanied by twisted leaves and abnormal growth. From the high percentage of ash (tables 2 and 3) the injury was apparently due to solution balance and increased permeability. Series III showed abnormal growth with no chlorosis.

Dates of heading (table 1) indicate that a high proportion of the phosphorus-potassium salt to low nitrogen, as found in series II and III, causes earlier maturity.

A part of the cultures was transferred on March 28 to 4-gallon jars to check the response to increased volume of solution culture and increased root space. They resumed growth, indicating that small containers might be a limiting factor in sand culture experiments.

None of the solutions tested produced grain normally under the conditions of the experiment. A high ratio of calcium nitrate to potassium di-hydrogen phosphate seems to have increased tillering and caused a heavy succulent growth. Series III, with the high proportion of potassium di-hydrogen phosphate, produced the heaviest root growth, series I intermediate, and series II the lowest. Root growth was checked in series II by injury probably due to the physiological balance of the solution. The apparent effect of the high

proportion of potassium di-hydrogen phosphate to a low calcium nitrate is a decreased top growth and a heavy root growth. The plants produced are of such a nature as to be economical in the use of water.

Chemical determinations show that Ca, K, P, and S are absorbed in proportion to the concentrations of these elements in solution. Increased potassium apparently decreased the absorption of magnesium. Iron and aluminum were practically constant in the ash of all plants. A slightly lower percentage of nitrogen in series I over series II indicates that high calcium concentration might inhibit the absorption of the NO_3^- ion.

Total ash was high in all series, but was very high in series II, the one showing the most chlorosis and injury. The plants grown in series I were highest in yield of dry matter and lowest in total ash.

Apparently growth abnormalities and low yields were due to the unusually high absorption of the mineral elements in solution.

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THE RATIO OF SULFUR TO PHOSPHORUS IN WESTERN OREGON SOILS AND LOSSES OF SULFUR THROUGH DRAINAGE AND CROPPING¹

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With comparatively little effort one might compile a very extensive bibliography of recently reported researches and reviews bearing on the rôle of sulfur in soil fertility and plant growth. The evidence is strong in support of the idea that sulfur fertilization frequently is the key to profitable crop production. There should no longer be hesitancy in extending, by the addition of sulfur and sulfur carriers, the list of commercial fertilizers, which once was thought to be complete with the naming of nitrogen, phosphorus, and potassium carriers. The Oregon state fertilizer control law gives sulfur and some of its compounds this important recognition.

SULFUR, NOT PHOSPHORUS, THE LIMITING FACTOR IN THE MEDFORD AREA

The use of sulfur for fertilizing purposes in Oregon dates from the attempts of Reimer and Tartar in 1912-14 to demonstrate in Jackson County (Rogue River Valley) the utility of phosphate applications for the growth of alfalfa on certain soil types whose chemical analysis revealed what appeared to be a low content of phosphorus. For reasons fully stated (6), these men slowly were forced to the conclusion that the remarkable results they had secured in the growth of alfalfa from their first application of superphosphate were due solely to its sulfur content. Their subsequent carefully planned experiments, together with those initiated by Powers in Central Oregon in 1913 and in the Willamette Valley in 1914, have established beyond all question the fertilizing value of sulfur and sulfur carriers for very extensive areas of Oregon (5). It is appropriate to add that the work of Olson and St. John leads unmistakably to the conclusion that sulfur likewise functions very strikingly as a fertilizing element on many types of soil in the state of Washington (4). The more recently reported researches of Miller at the Oregon Experiment Station make it plain, that, although sulfur and its compounds, by stimulating the activities of legume bacteria, function indirectly in the soil as fertilizing agents, they function directly just as strongly in supplying to growing crops an essential element of plant nutrition (3).

¹ Approved for publication by the experiment station committee on soil research.

² Chemist in charge, division of agricultural chemistry.

Reimer and Tartar began their fertilizer field tests in the Rogue River Valley in the absence of complete chemical data for the various soil types previously mapped by the Bureau of Soils in its survey of the Medford area. Had they been in possession of complete information regarding the chemical composition of the soil types of that area, a line of reasoning similar to that employed for phosphorus might have been directed toward sulfur. In that case they might have reached much sooner than by the empirical methods employed, their final conclusions relative to the need of those soils for additional sulfur. While their fertilizer trials were in progress, however, complete analyses were made of the most prominent soil types of the Medford area embracing a total of approximately 544 square miles. The results were published in 1920 (10). Since then, chemical analyses of predominating soil types have been made of all areas in Oregon completed by soil survey parties.

THE RATIO OF SULFUR TO PHOSPHORUS

Tartar and Reimer found for the soils of the Medford area smaller amounts of sulfur relative to phosphorus than have been reported by Hart and Peterson of Wisconsin (2), Shedd of Kentucky (8), Brown and Kellogg of Iowa (1), Swanson and Miller of Kansas (9), and by Robinson of the United States Department of Agriculture (7). The reason apparently lies chiefly in the smaller content of phosphorus in the soils reported by these investigators, not in an appreciably larger content of sulfur. For 27 types of the Medford area Tartar and Reimer found the maximum sulfur and phosphorus content of the surface soils to be 980 and 2180, respectively, expressed as pounds in 2,000,000 pounds of soil. The minimum amounts, expressed in the same way, were 300 and 900. The averages for the 27 types were 620 and 1420. The averages give a ratio of sulfur to phosphorus of 1 to 2.3. The Medford area has insufficient rainfall to make general farm and orchard practice profitable without irrigation. It will be noted that the ratio of sulfur to phosphorus is much narrower for this area than for the humid areas of the Willamette Valley.

THE WILLAMETTE VALLEY

Areas most recently surveyed in Oregon on the basis of the coöperative agreement prevailing between the Bureau of Chemistry and Soils of the United States Department of Agriculture and the Oregon Agricultural Experiment Station, comprise in total what is known geographically as the Willamette Valley. This valley includes that portion of northwestern Oregon which lies on the west slope of the Cascade range of mountains, the east slope of the low Coast range, and the wide expanse of level land between, through which the Willamette River flows on its way to join the Columbia River below the city of Portland. Roughly speaking, the valley is from 160 to 175 miles long and from 60 to 75 miles wide. Nine large counties constitute the political divisions of the valley. All have had their cultivatable lands classified and mapped

by type. The basis of soil classification is pedographic development. Practically every type of soil mapped has been represented in the chemical laboratory, as the field work progressed, by well-chosen samples taken in each of the counties in which it occurs. This paper concerns itself only with the relative abundance of sulfur and phosphorus as revealed by analytical work.

The arable soil types of the valley permit of grouping into four major divisions; namely, residual, old valley filling, recent alluvial, and peat. Each of the first three groups consists of a number of soil series of similar origin geologically, and of like topography, color, drainage, and subsoil. Again, each of the several series includes a number of types that differ one from the other in texture only.

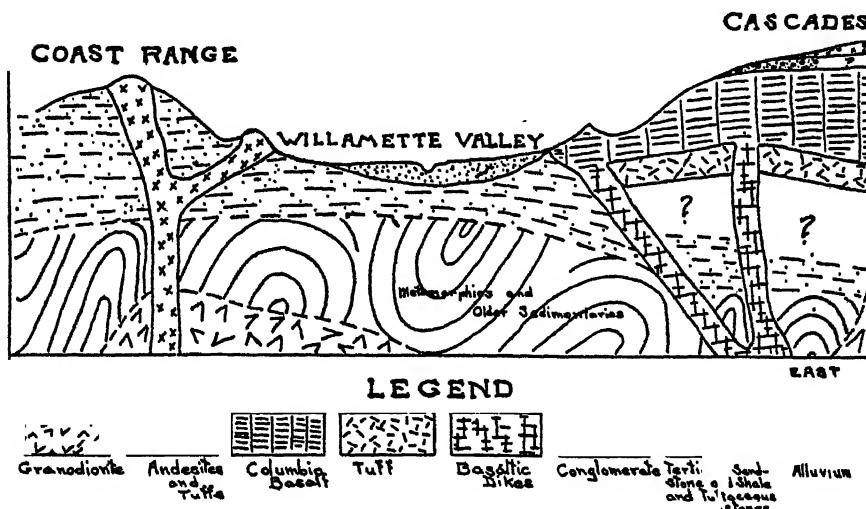


FIG. 1. SECTION WILLAMETTE VALLEY—AFTER WARREN DU PRE SMITH

Figure 1 is an ideal cross section of the lower end of the valley illustrating its predominating geological characteristics and in a measure the relative positions of the several groups of soils. It is unnecessary for the immediate purposes of this paper to reproduce here the original and detailed tabulation of analytical data by soil series and types under the group divisions indicated above. Table 1 is a condensation of that tabulation.

This summary of detailed analytical data makes it perfectly plain that the ratio of sulfur to phosphorus in Willamette Valley soils is much wider than Tartar and Reimer found for the soils of the Medford area in the semi-arid Rogue River Valley. It is much wider still than the ratios recorded for certain Eastern and Middle Western areas by other investigators mentioned earlier in this

TABLE 1
A summary of analytical data for sulfur and phosphorus in Willamette Valley soils

GROUP AND ORIGIN	POUNDS PER 2,000,000 POUNDS OF SOIL	
	Sulfur	Phosphorus
1. Residual (Red Hill Soils).....		
(a) Igneous Division (Basaltic)		
Maximum.....	1,040	6,200
Minimum.....	80	860
Average—S in 34 soils; P in 32.....	435	2,423
Ratio of averages.....	1	5.6—
(b) Sedimentary Division (Shales and Sandstones).....		
Maximum.....	860	3,060
Minimum.....	120	1,060
Average—S in 26 soils; P in 28.....	381	1,719
Ratio of averages.....	1	4.5
2. Old Valley Filling		
(a) Basaltic and Sedimentary		
Maximum.....	980	6,120
Minimum.....	100	840
Average—S in 87 soils; P in 86.....	433	2,366
Ratio of averages.....	1	5.5
(b) Sedimentary		
Maximum.....	700	2,440
Minimum.....	260	1,300
Average—S in 3 soils; P in 3.....	500	1,847
Ratio of averages.....	1	3.7
3. Recent Alluvial		
(a) Basaltic and Sedimentary		
Maximum.....	1,560	3,840
Minimum.....	120	800
Average—S in 74 soils; P in 71.....	450	1,864
Ratio of averages.....	1	4.1
(b) From Mixed Rocks		
Maximum.....	940	2,440
Minimum.....	230	1,440
Average—S in 4 soils; P in 4.....	647	1,905
Ratio of averages.....	1	3.0
(c) From Basaltic Rocks		
Maximum.....	940	3,700
Minimum.....	190	860
Average—S in 6 soils; P in 6.....	488	2,190
Ratio of Averages.....	1	4.5
4. Peat		
Maximum.....	5,740	2,060
Minimum.....	3,180	1,800
Average—S in 4 soils; P in 4.....	4,460	1,940
Ratio of Averages.....	2.3	1

paper.³ The reasons appear to be a somewhat lower sulfur content in Willamette Valley soils and a much higher phosphorus content. The higher phosphorus content is reasonably to be anticipated inasmuch as many of the Willamette Valley soils are derived wholly or in large measure from basaltic rocks. Soils of the Medford area are derived largely from granites, sandstones, and shales. The peat soils of the Willamette Valley, exceedingly rich in sulfur and by no means low in phosphorus, reverse the predominant relationship of these two soil components.

TABLE 2

The sulfur and phosphorus content of some commonly grown legumes, forage crops and grains

CROPS, WHERE GROWN, AND NUMBER OF DETERMINATIONS	SULFUR	PHOSPHORUS
	(DRY)	(DRY)
Alfalfa, Willamette Valley.....	7	0.160
Alfalfa, Rogue River Valley.....	4	0.182
Clover, Red, Willamette Valley.....	16	0.093
Clover, Red, Coast Section.....	2	0.093
Clover, Red, Rogue River Valley.....	3	0.141
Clover, Alsike, Willamette Valley.....	5	0.114
Clover, Alsike, Coast Section.....	4	0.110
Vetch, Willamette Valley.....	22	0.095
Peas, Willamette Valley.....	3	0.103
Peas, Coast Section.....	1	0.139
Timothy, Willamette Valley.....	3	0.075
Orchard Grass, Willamette Valley.....	1	0.048
Sunflowers, Willamette Valley.....	1	0.127
Wheat (grain), Willamette Valley.....	1	0.121
Wheat (grain), Rogue River Valley.....	2	0.131
Oats (grain), Willamette Valley.....	3	0.148
Barley (grain), Willamette Valley.....	2	0.117
Barley (grain), Rogue River Valley.....	2	0.110
Corn (grain), Willamette Valley.....	1	0.121

INFLUENCE OF DRAINAGE AND CULTIVATION ON THE RATIO OF SULFUR TO PHOSPHORUS

In view of what is known by experimental evidence to be taking place in all soils through the operation of natural agencies and agricultural practices, we must assume for the soils of the Willamette Valley in the early stages of their development a much higher sulfur content than is now characteristic of them. Of natural agencies, the heavy annual rainfall (40 to 50 inches) operates most

³ In this connection, however, one should note that Eaton in a contribution to *Botanical Gazette*, calls attention to several areas of Eastern and Midwestern soils whose ratio of sulfur to phosphorus is much wider than that recorded by other investigators already noted. The difference in all cases is due principally to a higher phosphorus content. See EATON, S. V. 1922. Sulfur content of soils and its relation to plant nutrition. *Bot. Gaz.* 74: 32-54.

noticeably to widen the ratio of sulfur to phosphorus. This statement is based in part upon analytical data for sulfur in the percolate from a lysimeter tank filled with an Old Valley filling soil. Three years' data indicate an average annual loss of 15 pounds of sulfur per acre from a 4-foot depth of this soil when untreated. When the soil is fertilized with barnyard manure or when treated with limestone, the annual losses of sulfur by natural leaching were substantially greater. A study of data resulting from analyses of drainage waters, whether natural or induced by irrigation, as in semi-arid regions, leads to the same conclusion: Wherever water escapes from the soil it carries with it a large amount of sulfur that previously was a soil component. The loss of soil phosphorus, through drainage, in comparison with sulfur is inappreciable.

The drain upon soils for sulfur and phosphorus by the annual growth and removal of farm crops in each case is large. From the data given in table 2 one can readily determine and express it on the basis of pounds per acre per unit of crop harvested. The most commonly grown crops of the Willamette Valley remove annually from one-third to two-thirds as much sulfur as is lost through drainage from the acreage that grew them. It is plain, too, that the drain upon sulfur annually by cropping is less than the drain upon phosphorus. Since the amount of sulfur brought to earth annually by rainfall here is less than ten pounds per acre, it appears fair to conclude that the combined losses of sulfur sustained annually by the soils of the Willamette Valley through leaching and the removal of farm crops are greater than the annual loss of phosphorus. Cultivation possibly offsets in a measure the effect of natural agencies operating to widen the ratio of sulfur to phosphorus. However, since most soils of the Willamette Valley have been under cultivation for a period not exceeding six or seven decades, the leaching effect of rainwater through centuries of time has been the predominant factor in determining for them the prevailing ratio of sulfur to phosphorus.

TOTAL AMOUNTS OF SULFUR AND PHOSPHORUS OF FIRST IMPORTANCE

In this presentation and discussion of analytical data it may appear to some that the ratio of sulfur to phosphorus in soils has been too greatly stressed. As a matter of fact, no particular ratio of these two elements is indicative of optimum conditions from the standpoint of soil fertility. Absolute amounts of each element, however, are considerations of first importance. The primary purpose of this paper is a presentation in as condensed form as possible of additional data bearing upon the actual amount of sulfur present in the soils of Oregon together with the best local information available on losses of sulfur from soils annually by drainage water and the removal of farm crops. In mentioning the sulfur to phosphorus ratio, advantage merely is taken of an opportunity to point out wherein two generalizations somewhat current in soil literature do not hold. First, for at least two very extensive areas in western Oregon, the soils' content of sulfur never approximates their phosphorus con-

tent. Second, the commonly grown legumes, forage grasses, and grain in these areas do not draw upon the soils so heavily for sulfur as for phosphorus. Finally, in the fact that the sulfur content of these two and other soil areas in Oregon is substantially lower than the phosphorus content and the total amount removed annually by natural or induced drainage is larger, lies sufficient reason for the unusual attention given sulfur in this state in fertilizer trials.

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SEWAGE SLUDGE AS FERTILIZER¹

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Human wastes and wastes from certain industrial processes contain considerable quantities of plant-food, which under ordinary conditions are lost. If the sewage is not treated, the material finds its way into streams and water courses; and in those cases where sewage disposal plants are present, the organic solids are retained as a sludge.

There are two general methods of sewage purification; namely, settling of solids followed by anaerobic digestion, and oxidation by forcing air into sewage. In both cases quantities of sludge are left behind. The sludges contain appreciable quantities of nitrogen and some phosphorus and potash, but the chief value of the sludge for fertilizer is in its nitrogen content.

There is at present only one sewage disposal plant in this country—the Milwaukee Activated Sludge Sewage Plant—where sludge is commercially marketed on a large scale. In a number of instances the sludge is locally sold for a nominal sum to farmers in the neighborhood. In the majority of cases the sludge is either buried or used for filling-in low places.

COMPOSITION

The product sold by Milwaukee under the trade name of "Milorganite" has been dried, finely and evenly ground, and contains 5 per cent or less moisture.

Kadish (2) has published an analyses of the material, representing 145 carloads shipped during a part of 1927. The composite sample contained:

	<i>per cent</i>
Total nitrogen.....	5.42
Water soluble organic nitrogen.....	0.30
Nitrogen insoluble in neutral permanganate.....	0.71
Active nitrogen by alkaline permanganate.....	3.22
Total phosphoric acid.....	3.08
Available phosphoric acid.....	2.43

There are only a few activated sludge sewage disposal plants in the country as compared with disposal plants where the sludge is digested anaerobically. Sewage sludge loses part of its nitrogen content in the course of digestion, probably most of it as nitrogen gas. As examples of the fertilizing value of

¹ Paper of the Journal Series, New Jersey Agricultural Experiment Station, Department of Sewage Disposal.

fresh (undigested) solids, partially decomposed material, and fairly well-digested sludge, analyses of material obtained from the Joint Sewage Disposal Plant of Dunellen, Plainfield, and North Plainfield, New Jersey, are given in table 1. The analysis used for illustration show a rather high initial total nitrogen content. It usually runs at this particular plant between 3.50 to 4.00 per cent nitrogen. An average of a number of analyses shows 3.62 per cent total nitrogen in the fresh solids and 2.70 per cent in the ripe (digested) sludge.

At the request of the author, a number of superintendents and engineers in charge of sewage disposal plants in the country forwarded samples of sludge to our laboratory for analysis. The pertinent results together with some remarks are given in table 2. The percentage ash of the materials varies considerably. There are two reasons for this variation; namely, inorganic

TABLE 1
Analysis of Plainfield sewage sludge

	FRESH SOLIDS	PARTLY DI-GESTED SOLIDS	FAIR DIGESTED SOLIDS
	per cent	per cent	per cent
Total N.....	4.81	3.98	3.55
Insoluble N.....	4.14	3.61	3.41
Soluble N.....	0.67	0.37	0.14
NH ₃ -N.....	0.09
Soluble organic N.....	0.05
Active insoluble N.....	0.98	1.89	1.57
Inactive insoluble N.....	1.16	1.71	1.84
Ether extract.....	15.11	7.79	6.83
Crude fiber.....	6.01	5.55	5.50
Ash.....	25.70	37.90	42.62

trade wastes present in the sewage, and the degree of decomposition accomplished. Domestic wastes settling out at a sewage treatment plant contain from 20 to 25 per cent ash. These solids, kept for a considerable number of days in digestion tanks, decompose under anaerobic conditions, producing large quantities of methane, some carbon dioxide, and some nitrogen gases (CH_4 , 70 to 75 per cent; CO_2 , 18 to 25 per cent; N, 3 to 10 per cent). The amount of ash remains constant but the percentage increases in relation to the percentage decrease of organic matter, with the result that well-digested sludge contains approximately 50 per cent ash. When inorganic trade wastes are received, the initial ash content varies from 25 to as high as 50 per cent, according to the amount of trade waste present.

The nitrogen content of the sludge depends upon the same two factors. The better digested, the lower the nitrogen content; and the more trade waste, the less the original percentage nitrogen, except when slaughterhouse, tannery,

and such wastes are treated. If less than 2.5 per cent total nitrogen is present in the digested sludge there is ordinarily inorganic trade waste present.

The sewage plant operator wishes to produce a well-digested material, because this material will dry rapidly and has no odor, but in doing so, the fertilizing value of the sludge decreases.

The amount of dry domestic solids produced per capita per day is fairly constant. A large number of analyses shows it to be in the neighborhood of 70 gm. per capita daily. With trade wastes present the amounts rise sometimes as high as 200 gm. per person per day. The amount of solids retained

TABLE 2
Analysis of sludge from different disposal plants

PLACE	TOTAL N	ASH	DEGREE OF DIGESTION
	per cent	per cent	
Trenton, N. J.....	1.18	51.7	Good
Rochester, N. Y.....	1.96	59.1	Good
Schenectady, N. Y.....	1.86	56.9	Fair
Schenectady, N. Y.....	1.97	44.1	Poor
Fort Worth, Tex.....	2.77	31.5	Poor
Fort Worth, Tex.....	2.07	48.4	Fair
Marion, O.....	2.70	48.1	Fair
Marion, O.....	2.49	46.9	Good
Baltimore, Md.....	2.48	32.1	Poor
Baltimore, Md.....	2.18	50.5	Good
Portsmouth, O.....	0.63*	81.9*	Much sand
Chambersburg, Pa.....	2.53	38.2	Poor
Mount Alto, Pa.....	1.70	41.2	Fair
Lebanon, Pa.....	2.68	40.4	Fair
Worcester, Mass.....	2.97	36.9	Fair
Chicago, Ill.....	1.67	58.4	Good
Antigo, Wis.....	2.09	55.2	Good
Plainfield, N. J.....	3.16	37.2	Fair
Plainfield, N. J.....	2.56	49.8	Good
Average.....	2.28	45.4	

* Left out of average.

at a domestic sewage treatment plant varies from 30 to 65 gm. per capita per day, depending upon the type of treatment plant. In the aggregate the quantities of sludge produced are enormous. Milwaukee alone, for instance produces approximately 25,000 tons of dry sludge, which must be handled in a wet condition, requiring machinery to treat 500,000 tons sludge. Where the sludge is digested, the quantities are lower. Fuller and McClintock (1) state that at present about 15 per cent of the sewage is treated in this country. The total dry solids in the sewages received at these plants is between 400,000 and 500,000 tons per year. Assuming a minimum average of 2 per cent nitro-

gen in the sludge, the annual loss of nitrogen amounts to from 8,000 to 10,000 tons for the treated sewage only. Most of this could be used as fertilizer, since it is already collected at sewage disposal plants.

From 150,000 to 200,000 tons of nitrogen, as a conservative estimate, present in sewage is annually lost by discharging sewage into streams and water courses, and by wasting the sludges.

SUMMARY

The nitrogen content of sewage sludges varies with the type of treatment. Aerobically treated sewage sludge contains about 5 per cent, and anaerobically treated sludge averages about 2.25 per cent nitrogen. Only one sewage treatment plant markets its sludge on a large scale; at a number of places the sewage sludge is given away or sold for a small nominal sum. It is estimated that from 150,000 to 200,000 tons nitrogen is lost annually. Based upon analysis of a number of sludges from different sewage plants, it is estimated that from 8,000 to 10,000 tons nitrogen per year could be saved at present.

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THE HYDROGEN PEROXIDE-HYDROCHLORIC ACID TREATMENT OF SOILS AS A METHOD OF DISPERSION IN MECHANICAL ANALYSIS

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At the Rothamsted meeting in 1926 the physics commission of the International Society of Soil Science discussed the hydrogen peroxide-hydrochloric acid method (method A) of pre-treatment of soil for the pipette method of mechanical analysis and recommended its adoption by the society as the approved international method (2). This proposal was adopted with only a few minor alterations at the Washington Congress in 1927 (5).

During an investigation of certain hardpan soils of California, the international method A proved inadequate as a means of dispersal for mechanical analysis. The study here reported was accordingly undertaken for the purpose of comparing the hydrogen peroxide-hydrochloric acid treatment with a simpler means of aggregate dispersion, as to their effects upon the yield of various fractions from certain selected soil types when analyzed by the pipette method.

CHARACTERISTICS OF THE SOILS USED

In addition to a hardpan soil from the group mentioned above, four other soils were selected as special types which might be expected to be greatly influenced in apparent physical composition by one or other of the two analytical methods under comparison. The characteristics of these five soils are given in table 1. They were selected because of their high organic matter content, soil O, Montezuma clay adobe surface, 0-14 inches depth, dark brownish gray color, from near Santa Rita, California; high lime content, soil L, Montezuma clay adobe subsoil (of soil O), 32-40 inches depth, light gray color; high sodium carbonate content, soil A, Fresno sandy loam ("black alkali soil") surface, 0-12 inches depth, light grayish brown color, from Kearney Park, California; apparently highly ferruginous nature, soil F, Aiken clay loam subsoil, 12-14 inches depth, rich brownish-red color, from near Camino, California; and difficulty dispersible nature, soil J, San Joaquin sandy loam hardpan horizon, 25-30 inches depth, pinkish-brown color, from near Clements, California; respectively.

DESCRIPTION OF METHODS OF ANALYSIS

The soils, which had been stored in glass jars for several months, were approximately air-dry. The larger aggregates were broken down with care and the soils sifted with a 2-mm. sieve having round holes. Moisture determinations at 105° to 110°C. were then made upon sub-samples of the thoroughly mixed fine earth, and the necessary amounts of the air-dry material weighed out into beakers to give the equivalent of 5 gm. of dry soil in every case. The pipette method of G. W. Robinson (8) was followed in making all the mechanical analyses, but in order to facilitate interpretation of results in the terms of the Bureau of Chemistry and Soils the same separate sizes and fraction names adopted by that Bureau were used, except that the clay was separated

TABLE I
Characteristics of soils used

SOIL	pH*	LOSS IN WEIGHT DUE TO TREATMENT WITH HYDROGEN PEROXIDE	CaCO ₃ CONTENT CALCULATED FROM AMOUNT OF 0.0938N HCl CONSUMED (6) ON HEATING	MOISTURE EQUIVALENT	WATER VAPOR ABSORBED OVER 3.3 PER CENT H ₂ SO ₄ IN GRAMS PER GRAM OF SOIL FINER THAN 2 MM.	AMOUNT† OF SESQUIOXIDES AND SILICA REMOVED BY 0.2N HCl DURING ANALYSIS BY METHOD (I)
O	7.6	per cent	per cent	per cent	per cent	per cent
L	8.2	4.7	9.08	28.7	0.113	0.92
A	...‡	2.1	1.03	26.6	0.105	0.81
F	7.0	1.3	0.54	10.9	0.161	0.23
J	7.7	0.11	1.09	38.6	0.206	0.40
		0.48		12.9	0.077	0.32

* Determined colorimetrically.

† By single precipitation with NH₄OH, and ignition.

‡ Not determined due to dark shade of aqueous extract. Salt content over 1500 parts per 100,000.

O—Montezuma clay adobe, 0-14 inches.

L—Subsoil of O, 32-40 inches.

A—Fresno sandy loam, "black alkali soil," 0-12 inches.

F—Aiken clay loam subsoil, 12-14 inches.

J—San Joaquin sandy loam hardpan horizon, 25-30 inches.

into two fractions, the coarser including particles .005 to .001 mm. size and the finer including those particles below .001 mm. effective diameter.

Method 1

In the first of the two methods of pre-treatment of the sample the international method A (2, pp. 5, 6) involving the use of hydrogen peroxide and hydrochloric acid, was followed very closely. No exact amount of soil is there given for analysis. Accordingly, no prescribed proportions of soil and hydrogen peroxide can be taken. Five-gram samples of soil were used, and as a guide to the proportions of soil to hydrogen peroxide necessary for complete decomposition of organic matter, reference was made to the conclusions of

W. O. Robinson (10, p. 341). For the obviously most highly organic of the five soils (soil O) the equivalent of 100 cc. of 15 per cent hydrogen peroxide to 5 gm. of soil was used. For the remaining four distinctly less organic soils the equivalent of 30 cc. of 15 per cent hydrogen peroxide was added to each 5 gm. sample of soil.

The beakers containing the mixture were placed on the steam-bath and digested for 2 hours, and then allowed to cool. The volume of the mixture was next adjusted with distilled water to give in a final volume of about 250 cc. a concentration of 0.2 N hydrochloric acid upon the addition of the necessary amount of normal acid. The amount of 0.2 N hydrochloric acid decomposed by the soil constituents at room temperature had already been determined with separate samples and allowance for this was made. The beaker and contents were allowed to stand for one hour, the supernatant liquid was decanted on to a filter and finally the soil itself entirely transferred on to the filter. The filter contents were then washed with distilled water until no chlorides were obtained in the wash water of any except that from the fine textured soils O and F. Traces of chloride persisted in the filtrate from these after long continued washing. To the filtrate obtained after the peroxide-hydrochloric acid treatment ammonium hydroxide was added and a proximate determination of dissolved sesquioxides and silica made after a single precipitation and ignition. The contents of each filter were then washed into two 300-cc. shaker bottles, and 1 cc. of 28 per cent ammonia solution added to the contents of each bottle in a volume of 150 cc. The bottles and their contents were shaken for 15 hours on a horizontal reciprocating shaker, and transferred by means of a strong jet of distilled water to tall glass cylinders, each 5-gm. sample of soil being made up to a volume of 500 cc. After withdrawal of the silt and clay portions, the cylinders were protected from temperature changes and from light by a thick-walled wooden box. Maximum fluctuations in temperature of only 1° to 2°C. occurred. Sampling with a single orifice 20-cc. pipette was carried out after the appropriate intervals of time in each case. The various samples containing the material finer than 50, 5, and 1 μ diameter, respectively, were run into freshly dried and weighed 50-cc. Pyrex beakers or weighing bottles (the latter were used entirely for the suspensions of finest material), placed in an oven at 105° to 110°C. for 48 hours, and then weighed. From the known concentration of the original suspension the percentages of these finer particles were calculated. After the withdrawal of the particles of diameter less than 1 μ , the sediment containing the coarse fractions was transferred to a 0.1-mm. mesh silk sieve, most of the very fine sand and all of the finer material being washed through. The sands retained by the screen were then removed, dried, and returned to a nest of sieves and shaken mechanically for 15 minutes, after which the separate fractions were weighed. The very fine sand was obtained by difference after allowance had been made for the organic matter, and sesquioxides plus silica, removed by the hydrogen peroxide and hydrochloric acid.

The amount of calcium carbonate dissolved at room temperature upon the addition to the soil of 0.2 *N* hydrochloric acid, calculated upon the assumption that the amount of acid consumed reacts entirely with calcium carbonate, amounted in the case of soil L, the most calcareous of the five, to 1.27 per cent. Such an assumption is erroneous, for sesquioxides and silica were removed from this soil to the extent of 0.81 per cent by the acid treatment. Since the correction would be slight for any of the soils and since the proportions of different carbonates, sesquioxides, and silica, which decompose the acid, can be determined only by more complete analyses, no correction has been made for the dissolved carbonate content in computing the very fine sand fraction, which must be recognized to be slightly increased in amount on this account.

Method 2

In the second method used, the pre-treatment consisted of rubbing the soil sample in an agate mortar with a rubber tipped pestle for 10 minutes. The soil was immersed in a very dilute solution of ammonia (1 part ammonia to 3000 parts water) during this process of trituration. Each sample was then transferred to a shaker bottle and shaken with water to which ammonia had been added, as before, for 15 hours. From this point the treatment was identical with that followed in method 1, except that all withdrawn samples and separates were treated with 25 cc. of 3 per cent hydrogen peroxide in order to remove the organic matter before weighing.

DISCUSSION

Table 2 contains the results of analyses by methods (1) and (2). The average summation percentages for the two methods have been arranged in table 3, and from these data the summation curves of figure 1 have been plotted. For convenience in drawing the summation curves, it has been assumed that Stokes' law is valid for the sedimentation of soil particles of diameter greater than 50 μ and the logarithms of the settling velocities corresponding to the size limits of the various separates have been computed. These logarithmic values lie along the abscissa and the summation percentages along the ordinate in the figure. The average distribution percentages are given in table 4.

The nature of the possible modification of apparent soil properties is indicated in the following discussion.

Hydrogen peroxide-hydrochloric acid treatment before shaking

The peroxide removes practically all of the organic matter, both coarsely and finely divided. If Gile's definition (4, p. 361) of colloidal soil material is adopted, the colloid yield will thereby be reduced, but to that extent a correction may readily be made. By removal of the organic binding of fine mineral particles, the yield of inorganic colloids may be increased. The hydro-

TABLE 2
Results* of mechanical analysis of soils by means of the pipette-sedimentations method, using two different kinds of pre-treatment

PARTICLE SIZE	Colloidal clay		Clay		Silt + clay		Very fine sand		Fine sand		Medium sand		Coarse sand		Fine gravel	
	(i)	(ii)	(i)	(ii)	(i)	(ii)	(i)	(ii)	(i)	(ii)	(i)	(ii)	(i)	(ii)	(i)	(ii)
Pre-treatment	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent
soil	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent
O	28.1	15.0	36.9	31.1	69.4	70.4	17.5	16.6	6.1	5.8	0.64	0.55	0.63	0.76	0.24	0.29
L	26.2	14.4	32.3	26.7	66.4	69.7	23.5	20.0	6.2	6.7	0.46	0.40	0.39	0.30	0.22	0.07
A	3.7	7.5	7.8	36.8	34.2	27.0	33.4	18.2	16.3	3.4	3.0	8.0	7.4	5.2	4.1	
F	45.7	43.4	58.3	57.3	93.1	92.5	3.8	5.7	1.7	1.1	0.39	0.09	0.44	0.07	0.21	0.0
J	4.9	6.4	10.7	15.5	28.7	40.8	14.5	16.6	26.0	25.0	10.5	7.7	14.4	7.9	5.3	1.2

* Averages of duplicate determinations are given. In this and the following tables diameter sizes are calculated from the corresponding settling velocities derived from Stokes' law.

(i) Hydrogen peroxide-hydrochloric acid treatment before shaking.

(ii) Rubbing only with rubber pestle in dilute ammonia before shaking, separates later being treated with hydrogen peroxide before weighing.

TABLE 3
Average summations percentages, organic-matter-free material, for the fine soils examined by the two methods

Upper Limit of Particle Diameter	1 μ		5 μ		50 μ		100 μ		250 μ		500 μ		1000 μ		1000 μ	
	(i)	(ii)	(i)	(ii)	(i)	(ii)	(i)	(ii)	(i)	(ii)	(i)	(ii)	(i)	(ii)	(i)	(ii)
Log ₁₀ V*	5.98131	3.37925	3.37925	1.37925	1.37925	1.37925	0.77119	0.77119	1.37925	1.37925	1.98131	1.98131	2.58337	2.58337		
Pre-treatment method	(i)	(ii)	(i)	(ii)	(i)	(ii)	(i)	(ii)	(i)	(ii)	(i)	(ii)	(i)	(ii)	(i)	(ii)
soil	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent						
O	28.1	15.0	36.9	31.1	69.4	70.4	86.8	87.0	92.9	92.8	93.5	93.4	94.2	94.1	94.4	94.4
L	26.2	14.4	32.3	26.7	66.4	69.7	89.9	89.7	96.1	96.4	96.6	96.8	96.9	97.1	97.2	97.2
A	3.7	7.5	7.8	36.8	34.2	63.6	67.6	81.8	83.9	85.2	86.9	93.2	94.3	98.4	98.4	
F	45.7	43.4	58.3	57.3	93.1	92.5	96.8	98.2	98.5	99.3	98.9	99.4	99.3	99.5	99.5	
J	4.9	6.4	10.7	15.5	28.7	40.8	43.0	57.4	69.0	82.4	79.5	90.1	93.9	98.0	99.2	

calculated from Stokes' formula, where the velocity, $V = \frac{2}{9} \frac{g^2(s - s_1)}{\eta t}$ the various symbols having their usual significance, $t = 23^\circ\text{C}$.

Hydrogen peroxide-hydrochloric acid treatment before shaking.

Rubbing only with rubber pestle in dilute ammonia before shaking, separates later being treated with hydrogen peroxide before weighing.

chloric acid treatment will decompose a small proportion of the calcium carbonate, and other soluble carbonates present, and also very small quantities of fine silicates and oxides. More important than this is the partial replacement of absorbed cations by hydrogen ion, and the fairly complete removal of replaced ions by washing. An artificial podsolization process is thus carried out upon the soil, and opportunity provided for great alteration in the nature of the electrical double layer of the acidoid part of its colloidal fraction. To the extent that Ca and Mg ions are removed dispersion will be aided. Removal of the more readily hydrated Na ion, and of K ion will tend to hinder

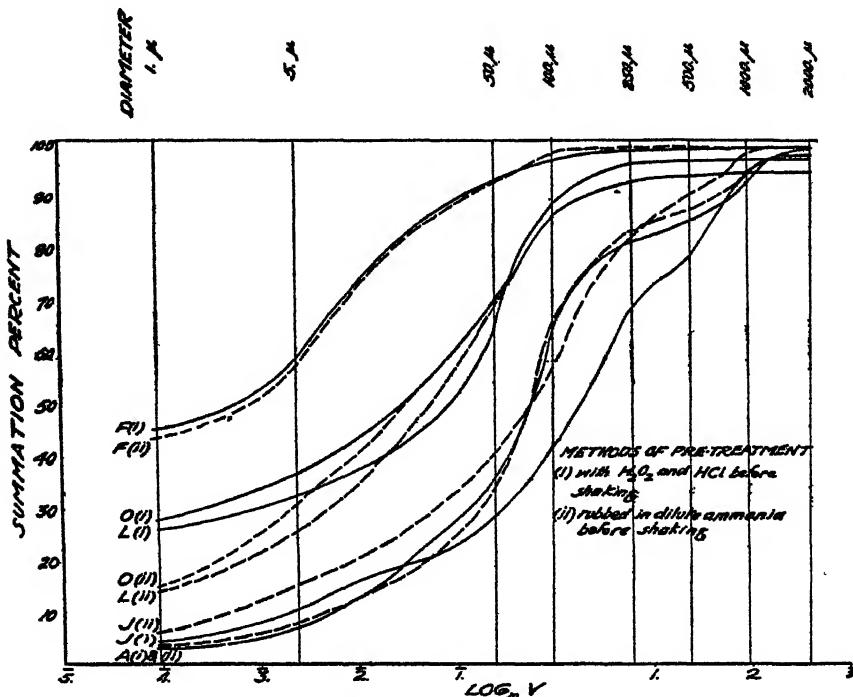


FIG. 1. SUMMATION CURVES FOR FIVE SOILS

ultimate dispersion. Wiegner (11) has pointed out how even the size of the colloidal particles, and hence the shape of the distribution curve, may be affected by changes in hydration and imbibition as a result of treatment with electrolytes. Finally, thorough shaking in the presence of dilute ammonia water destroys aggregates and provides abundant ammonium ions, which, because of their hydration, help to decrease the probability of particle adhesion. It is evident that through all of these treatments the characteristics of the soil have been liable to severe modification, the extent of this being dependent upon soil variability, and being different for each soil.

TABLE 4
Average distribution percentages, organic-matter-free material, for the five soils examined by the two methods

DIAMETER.....	1 μ		1-5 μ		5-50 μ		50-100 μ		100-250 μ		250-500 μ		500-1000 μ		1000-2000 μ	
	Colloidal clay		Clay		Silt		Very fine sand		Fine sand		Medium sand		Coarse sand		Fine gravel	
	(i)	(ii)	(i)	(ii)	(i)	(ii)	(i)	(ii)	(i)	(ii)	(i)	(ii)	(i)	(ii)	(i)	(ii)
Pre-treatment method.....	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent
soil																
O	28.1	15.0	8.8	16.1	32.5	39.3	17.5	16.6	6.1	5.8	0.64	0.55	0.63	0.76	0.24	0.29
L	26.2	14.4	6.1	12.3	34.1	43.0	23.5	20.0	6.2	6.7	0.46	0.40	0.39	0.30	0.22	0.07
A	3.7	3.7	3.8	4.1	29.3	26.4	27.0	33.4	18.2	16.3	3.4	3.0	8.0	7.4	5.2	4.1
F	45.7	43.4	12.6	13.9	34.8	35.2	3.8	5.7	1.7	1.1	0.39	0.09	0.44	0.07	0.21	0.0
J	4.9	6.4	5.8	9.1	18.0	25.3	14.5	16.6	26.0	25.0	10.5	7.7	14.4	7.9	5.3	1.2

(i) Hydrogen peroxide-hydrochloric acid treatment before shaking.

(ii) Rubbing only with rubber pestle in dilute ammonia before shaking; separates later being treated with hydrogen peroxide before weighting.

Rubbing in slightly ammoniacal water before shaking

The aggregates will be mechanically dispersed to a great extent. Replacement by ammonium ions will occur to some extent in the absorbing complex, but a state of equilibrium will be reached between the added ammonium ions and the original absorbed cations due to lack of washing and to the presence of part of the original cations in the suspension. Stability of the suspension will usually tend to be increased. The opportunity for modification of soil characteristics is clearly less than with the peroxide-hydrochloric acid treatment, but here again the extent of modification will depend upon the inherent characteristics of the soil under examination.

Table 3 and the corresponding summation curves in figure 1 indicate the effect of the two methods of pre-treatment upon the apparent physical composition of the soils used in this comparison. In the case of the relatively highly organic surface soil O, dispersion was very incomplete for particles of less than 50 μ diameter, when no peroxide and hydrochloric acid were used. The undispersed colloidal clay appears to have been distributed uniformly between the coarser clay and the silt. The same holds true for the highly calcareous subsoil, L. The incomplete dispersion obtained by means only of trituration in ammoniacal water for these two soils is clearly shown by the depression of the summation curves in figure 1. Lack of dispersion by method 2 is probably attributable in the case of soil O to the presence of organic binding material and some absorbed calcium. The absorbed calcium alone was probably responsible for the incomplete dispersion of soil L.

No significant differences are apparent between the two methods in the case of the "black alkali" soil, A. Evidently it contained an amount of absorbed sodium of sufficient magnitude that any calcium displacement brought about by the peroxide-hydrochloric acid treatment was without effect upon its degree of dispersion. Soil F, the least alkaline of any examined, also proved to be equally affected by both treatments as far as measurable dispersion was concerned. Despite its ferruginous nature the amount of dissolved sesquioxides from this soil was low.

When the results obtained with soil J are compared for methods (1) and (2) however, the higher degree of dispersion obtained by the trituration method is very marked. All of the fractions below 100 μ diameter are depleted to the extent of from 10 to 30 per cent by the peroxide-hydrochloric acid treatment, whereas the coarser fractions have their percentages increased by such treatment, in some cases to as much as several hundred per cent of the amounts obtained by the trituration method.

In the present study, important differences in apparent physical composition were obtained with three out of five soils. For two of these a higher degree of dispersion was obtained by peroxide-hydrochloric acid pre-treatment, for one of them rubbing in dilute ammonia was the more effective in obtaining dispersion, while for the remaining two soils no significant differences were apparent.

Treatment with hydrochloric acid is theoretically severe. It is probable, however, that differences in particle size will involve a fluctuation frequently too slight to be detected when analysis is made by the pipette method, and on this account will usually be detected only when particle classes are numerous. In such a case as was presented by soil L above, a significant increase in the yield of fine particles was obtained upon treatment with hydrogen peroxide and hydrochloric acid. The question then naturally arises whether such dras-

TABLE 5

Content of colloidal matter as calculated by (A) sedimentation and (B) water vapor adsorption over 3.3 per cent sulfuric acid

PRE-TREATMENT METHOD.....	A COLLOIDAL MATTER CONTENT DETERMINED DIRECTLY BY SEDIMENTATION, ASSUMING STOKES' LAW (G. W. ROBINSON PIPETTE METHOD)				B COLLOIDAL MATTER CONTENT DETERMINED INDIRECTLY BY ADSORPTION OF WATER VAPOR OVER 3.3 PER CENT SULFURIC ACID (W. O. ROBINSON METHOD). SOIL MATERIAL GROUNDED TO PASS 0.1-MM. MESH SIEVE	
	Organic matter free*		Corrected for organic matter†			
	(i)	(ii)	(i)	(ii)		
soil	per cent	per cent	per cent	per cent	per cent	
O ₁	28.4	15.6	39.3	
O ₂	27.8	14.4	39.9	
Ave.	28.1	15.0	32.8	19.7	39.6	
L ₁	25.6	14.3	35.8	
L ₂	26.8	14.4	36.7	
Ave.	26.2	14.4	28.3	16.5	36.3	
A ₁	3.7	3.6	50.1	
A ₂	3.7	3.7	49.5	
Ave.	3.7	3.7	5.0	5.0	49.8	
F ₁	46.0	43.0	67.6	
F ₂	45.3	43.7	66.3	
Ave.	45.7	43.4	45.8	43.5	67.0	
J ₁	5.2	6.4	28.3	
J ₂	4.6	6.4	28.1	
Ave.	4.9	6.4	5.4	6.9	28.2	

* Finer than 1 micron diameter.

† Including organic matter, and inorganic material finer than 1 micron diameter.

(i) Hydrogen peroxide-hydrochloric acid treatment before shaking.

(ii) Rubbing only with rubber pestle in dilute ammonia before shaking, separates later being treated with hydrogen peroxide before weighing.

tic alteration of soil properties is allowable. How misleading is the distribution of particle size, obtained by this method of pre-treatment? When considering soils having a high degree of calcium saturation, as with soil L, the boundary line between particle size and particle arrangement is approached, but the accuracy of the picture of the physical constitution of such a soil, obtained by any method of pre-treatment involving severe alteration of the base exchange complex, is questionable, and the results obtained by sedimentation analysis then appear to lose much of their significance.

TABLE 6
The relationship of some "single-value" determinations to the content of colloidal clay and to each other

PRE-TREATMENT METHOD	MOISTURE EQUIVALENT	WATER ABSORBED IN 5 DAYS OVER 3.3 PER CENT H ₂ SO ₄ , EXPRESSED AS PERCENTAGE OF OVER-DRIED SOIL FINER THAN 2 MM.	RATIO: M.E. WATER ABSORBED	TOTAL COLLOIDAL MATTER (BY ABSORPTION METHOD)	RATIO: M.E. COLLOIDAL SOIL MATERIAL GROUNDED TO PASS A 2-MM. SIEVE	TOTAL COLLOIDAL MATTER CORRECTED FOR LOSS DUE TO PEROXIDE TREATMENT BY PIPETTE SEDIMENTATION METHOD		TOTAL COLLOIDAL MATTER		WATER ABSORBED OVER 3.3 PER CENT H ₂ SO ₄ TOTAL COLLOIDAL MATTER	
						(i)	(ii)	(i)	(ii)	(i)	(ii)
soil	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent
O	28.7	11.3	2.5	37.8	0.76	32.8	19.7	0.88	1.5	0.34	0.57
L	26.6	10.5	2.5	35.1	0.76	28.3	16.5	0.94	1.6	0.37	0.64
A	10.9	16.1	...	53.6	...	5.0	5.0	2.2	2.2
F	38.6	20.6	1.9	68.6	0.56	45.8	43.5	0.84	0.89	0.45	0.47
J	12.9	7.7	1.7	25.5	0.51	5.4	6.9	2.4	1.9	1.4	1.1

(i) Hydrogen peroxide-hydrochloric acid treatment before shaking.

(ii) Rubbing only with rubber pestle in dilute ammonia before shaking, separates later being treated with hydrogen peroxide before weighing.

WATER VAPOR ADSORPTION OVER 3.3 PER CENT SULFURIC ACID

All five soils were first ground to pass through a 0.1-mm. mesh silk sieve and were then exposed to water vapor for 5 days over 3.3 per cent sulfuric acid in partially evacuated, sealed desiccators. Duplicate soils were exposed in different desiccators. Unground samples of the same soils that had been passed through a 2-mm. sieve only were also exposed in a similar manner. The initial pressure within the desiccators averaged 5.5 cm. of mercury and was well maintained during the period of exposure. A constant temperature thermostat was not available at the time, and the desiccators were therefore placed in a thick-walled, light-proof, closed wooden box in the laboratory. The temperature within the box during the absorption period was recorded by means of a thermograph, and showed an extreme range of from 3° to 4°C., but considerably less than this during the 12-hour period immediately before removal.

The percentage content of colloidal matter, calculated by means of W. O. Robinson's formula (9) is given for each soil in table 5, and comparison is made with the percentages of organic-matter-free material finer than 1 μ in diameter and with the same plus-organic-matter as indicated by loss of weight due to peroxide treatment, both obtained by the pipette-sedimentation method when given two different kinds of pre-treatment. It will be observed that in every case the values obtained by the adsorption method are much higher, these increases amounting in some cases to several hundred per cent. There was relatively little difference obtained in the content of colloidal material when calculated by the adsorption method using soil material prepared by passing through a 2-mm. sieve and when the same soil had been ground to pass through a 0.1-mm. sieve previous to exposure in the adsorption chamber (see tables 5 and 6). The excessively high figure obtained for soil A is doubtless due to the high content of soluble salts present in the soil, and bears little direct relation to the true content of colloidal matter. The interrelationships existing between the various physical values determined for these soils are presented in table 6.

SUMMARY

The hydrogen peroxide-hydrochloric acid method of pre-treatment of soils for mechanical analysis was compared with the method of rubbing in dilute ammonia as means of dispersion for five different soils, and the effects of such treatments upon the apparent physical composition of soils were considered.

A much higher degree of dispersion, as measured by the yield of finer mineral fractions, was obtained for the rather highly organic soil used, and for its calcareous substratum, when treatment with hydrogen peroxide and hydrochloric acid preceded shaking. For the hardpan soil examined the peroxide-hydrochloric acid treatment was found to be entirely inadequate as a means of dispersion, and rubbing in dilute ammonia proved much more effective. A "black alkali" surface soil and an apparently highly ferruginous clayey soil horizon were equally well dispersed by both methods.

The advisability of subjecting calcium-saturated soils to the drastic treatment involved in the hydrogen peroxide-hydrochloric acid method is questioned.

Comparisons were made between the pipette-sedimentation method and the indirect water vapor adsorption method for the calculation of the content of so-called colloidal material, the latter method giving higher results in every case. Very fine grinding of the soil material had but relatively slight effect upon the amount of colloidal material, calculated by the water vapor adsorption method. The excessively high result obtained by the exposure of a black alkali soil to water vapor over sulfuric acid is pointed out. Interrelationships between the content of colloidal material and some "single-value" determinations are presented.

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SOME REACTIONS OF SEEDLINGS TO WEAK CONCENTRATIONS OF HYDROCHLORIC ACID AND CALCIUM

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It is the opinion of the writer that the distribution of plants in any geographical area cannot be explained on the basis of the cH¹ of the soil. That a great many factors operate in determining what the surviving flora will be, is generally admitted, but an extraordinary emphasis seems to be laid on the value of pH determinations.

Recently Wherry (15) attempted a classification of plant families according to their apparent preference for a given pH. The ferns and horsetails are found in soil with pH at about 6.5; the Ericaceae seem to thrive best on acid soils, as do the Saracinias and Dioneas; whereas the grasses as a group apparently prefer a "circumneutral" reaction. But especially with the ferns and grasses there are many exceptions. Saracinias are native to a light sandy soil. Such soils generally have a high potentiometric cH. It is worthy of note, however, that this same plant produces a more compact and sturdy growth in the Sphagnum bogs of New Jersey.

It would seem that pH is a corollary to other conditions which establish the nature of the flora rather than the immediate and direct cause. For, after all, cH is the result of already established equilibria.

The following experiment shows for *Agrostis alba*, var. *stolonifera*, Washington strain, an extremely great range of acid tolerance. White porcelain pots were filled with sand previously washed with HCl and distilled water. Five rooted stolons of *A. alba* were planted to each pot. Every second day, the nutrient already in each pot was drawn off and more added to make the water content equivalent to 60 per cent of the water-holding capacity of the sand. The preparation of the nutrient has already been described in a previous paper (11). The pH was varied by titrating the stock nutrient with KOH. The curve obtained was that determined by Clark (2). The plants were harvested after 24 days and the green and dry weights determined. The variation in the weights of the plants was less than 12 per cent for the pH controls used—3.7, 4.0, 4.5, 5.0, 5.5, 6.0. It was apparent that within these limits the concentration of the H-ion had little or no effect on the growth of the plants. It is pointed out, however, that all essential salts were present in their correct

¹ cH is the symbol for H-ion concentration. $pH = \log \frac{1}{cH}$.

antagonistic ratios. Such a condition would hardly obtain in a soil, especially at the lower pH.

It is the object of this paper to present some evidence as to the very different behavior of seedlings of *Lupinus albus* and *Phaseolus vulgaris nanus* to weak concentrations of Ca and HCl. These data sustain the opinion that soils of low pH may be toxic to some plants, not because of the H ion, but rather because of the absence of other ions in sufficient concentration.

ADAPTABILITY OF SEEDLINGS FOR EXPERIMENTS

In any toxicity experiments it is necessary to be dealing with cells normal with respect to food supply, and to have, as the only variable, the solution into which the seedlings are put. Hypogea, exaluminous seedlings are ideal for this work. When placed in tap water (having relatively little food value) such seedlings have sufficient reserve stored in their cotyledons to insure good growth for from seven to fourteen days, depending on the species and the temperature. It follows, then, that the cells at the periphery of the radical are supplied with the necessary elements for growth, not from the media, but from the cotyledons. Death or relative growth becomes a function of the media and not of starvation.

Seedlings of *L. albus* and *P. vulgaris nanus* are both epigeal and exaluminous. They were selected also because the former may be classed as a calciphobe and the latter as a calciphil. Lastly both species produce a strong straight radical at low temperatures.

EXPERIMENTAL METHOD

Seeds were germinated in large pots in sand until the radicals (not including the mesocotyl) were about an inch and a half long. They were well washed to free them of sand, quickly dried with filter paper, avoiding injury, and marked with India ink 5 mm. from the tip. They were then allowed to remain in distilled water for at least an hour before being used. Four seedlings were placed in parafined cork and cardboard tops which fitted tall liter beakers. The beakers were filled with appropriate solutions made by dilution from stocks used throughout the experiments. At the conclusion of every 24-hour interval, the solutions were changed and the growth of the radicals measured.

By means of a thermograph, temperatures were recorded for each experiment.

RESULTS

Table 1 shows the length attained in millimeters by the radicals at successive 24-hour intervals. The pH of each solution was determined by calculation and checked by taking the conductance of the solution and referring it to a curve obtained from the Landolt-Börnstein tables (7). This was believed more accurate than titrating, and certainly in such unbuffered solutions potentiometric determinations were not possible and the colorimetric method was unreliable for the accuracy desired.

The results show that lupines produce a better growth in distilled water than do beans. After the first day, the latter make no appreciable growth whatever, whereas lupines continue a steady though decreasing development. The response of lupines to small amounts of Ca is marked, but the benefit derived by Phaseolus is doubtful.

Table 1 indicates that significant growth is made with beans only in the presence of 5.0 p.p.m. Ca and that relatively none is observed in concentrations of 1.0 and 3.0 p.p.m. Ca. Further, that beans can tolerate a pH of 4.3 only in the presence of 5.0 p.p.m. Ca or more in which mixture a small but steady

TABLE 1
Length of radicals of L. albus and P. vulgaris nanus at 24-hour intervals
Average temperature, 24.0°C.

SOLUTION	LUPINUS ALBUS			PHASEOLUS VULGARIS NANUS			CONDITION OF SIDE ROOTS
	24 hours	48 hours	72 hours	24 hours	48 hours	72 hours	
	mm.	mm.	mm.	mm.	mm.	mm.	
Water.....	16	23	28	8.0	8.5	8.5
Ca 1 p.p.m.....	24	45	66	7.5	8.0	8.0
Ca 3 p.p.m.....	30	53	73	9.0	12.0	13.5
Ca 5 p.p.m.....	31	53	66	13.0	22.0	27.0
pH 4.1 (HCl).....	11.5	14	15.5	Dead	Killed
pH 4.2.....	14	18	21	Dead	Killed
pH 4.3.....	17	21	23.5	50 per cent	Normal	Killed
pH 4.5.....	17	22	26	9	10	10	Survive
pH 4.1 + Ca 1.....	15	21	27	Dead	Killed
pH 4.1 + Ca 3.....	18	25	31	Dead	Killed
pH 4.1 + Ca 5.....	17	25	35	Dead	Killed
pH 4.2 + Ca 1.....	13.5	20	27	Dead	Killed
pH 4.2 + Ca 3.....	16.5	24	36	Dead	Killed
pH 4.2 + Ca 5.....	22	34	46	Dead	Slowly killed
pH 4.3 + Ca 1.....	17.5	28	33	Dead	Slowly killed
pH 4.3 + Ca 3.....	19	37	48	Dead	Survive
pH 4.3 + Ca 5.....	25	47	62	7.0	7.5	8.5	Normal
pH 4.5 + Ca 1.....	20	33	48	8.0	8.5	8.5	Normal

growth is seen. Increasing the H ion concentrations results in the death of the radical tips even in the presence of 5.0 p.p.m. Ca. The toxicity of HCl to Phaseolus in the concentrations used is evident but that this is an additive injury is demonstrated later in this paper.

With lupines, however, the situation with respect to the so-called H ion toxicity is vastly different. For a period of 4 days, the radicals remain entirely normal in appearance in all solutions. Using as criteria of health the turgidity of radicals, loss of epidermis, turbidity of solutions, and color of radicals, no difference was detected in the radicals grown in the HCl solutions and those grown in CaCl_2 . The effect of the different solutions is seen only in the rates

of growth of the radicals. These data are given over a 3-day interval. In all cases an increase in growth is seen. At a cH of 0.00005, growth is at all times as good as in distilled water. When the cH is increased to 0.000063, the growth rate is very nearly as good as in distilled water. Further increase of cH to 0.000079 results in a significant growth depression but in no other apparent ill effects.

Adding as little as 1.0 p.p.m. Ca to the strongest HCl solution used, very nearly overcomes the depression observed in the lupines grown in HCl of the same concentration, whereas increasing the Ca concentration to 3.0 p.p.m. produces a growth normal with respect to distilled water. In weaker concentrations of HCl, the slight growth depression induced by HCl is obviated by additions of 1.0 p.p.m. Ca, and increasing the Ca concentration produces a growth approaching that attained by lupines in Ca alone.

TABLE 2
Length of radicals of L. albus and P. vulgaris at 24-hour intervals
Average temperature 20.0°C.

SOLUTION	P. VULGARIS NANUS			L. ALBUS		
	24 hours	48 hours	72 hours	24 hours	48 hours	72 hours
	mm	mm.	mm.	mm.	mm.	mm.
Water.....	7	8	8.2	16	22	26
Ca 0.5 p.p.m.....	7	8.2	8.5	17	31	45
Ca 1.0 p.p.m.....	9	10	11	22	40	55
Ca 3.0 p.p.m.....	8	11	13	30	53	61
Ca 5.0 p.p.m.....	13	22	27	31	53	58
Ca 10.0 p.p.m.....	17	31	45	30	50	60
Ca 33.0 p.p.m.....	19	38	61	31	51	58

To show the avidity of Phaseolus for Ca and the economy of lupines for the same element, the data in table 2 are presented.

Lupines make a decided growth in distilled water and profit greatly by Ca additions as dilute as 0.5 p.p.m. The maximum benefit of Ca to lupines is obtained at a concentration of 3.0 p.p.m. and further additions of this element, although not decreasing the rate of growth, do not increase it.

Practically no growth of the radical of Phaseolus is attained until the Ca concentration is 5.0 p.p.m. Increasing the amount of Ca added results in an increased growth rate.

During the winter of 1926-27, a rather detailed study was made of the soil near Paulsboro, N. J. In this region beans are widely grown and the soils in question produced the poorest crops of the immediate region. A composite sample of each soil was made from the surface 10 inches from ten locations. The pH was determined by the potentiometer, colorimetrically (using Brom-cresol-green) and titrimetrically with the quinhydrone electrode. The gravi-

tational and capillary waters were analyzed for Fe and Al gravimetrically and by the KCNS method. The gravimetric findings only are reported. The combined percolates of each soil were used in water cultures with beans and their toxic effect thus determined. The results are reported in table 3.

Using the pH of the soil extracts as criteria of relative toxicity, one would expect soils 3 and 4 to produce a much poorer crop than soils 1 and 2. This was not the case. Evidence to be presented in a later paper shows that the Fe determinations are very misleading. Although turbidity measurements were not made, it may be said that the Fe as analyzed is a function of turbidity. Unless the percolated extracts were boiled in HNO_3 before the addition of KCNS, no color was developed. From the evidence of table 2, the survival of Phaseolus in the soil with a pH of 3.8 is surprising. One series of results at first glance contradicts the other. But the data in table 3 make it clear that

TABLE 3

*Per cent increase in weights of *P. vulgaris* seedlings with respect to pH of percolates and other culture solutions and p.p.m. dissolved matter*

PERCOLATES	pH AVERAGE OF 8 TO 10 DETERMINATIONS	NUMBER OF SEEDLINGS	INCREASE IN WEIGHT	Fe IN PERCOLATES (NOT CENTRIFUGED)		DISSOLVED MATTER
				Gravita-tional water	Capillary water	
Soil 1.....	4.51	16	55	0.170	1.700	325
Soil 2.....	4.60	14	65	0.180	0.640	310
Soil 3.....	3.80	15	50	0.013	0.093	150
Soil 4.....	3.90	16	54	0.018	0.050	200
Distilled water.....	6.10	11	9
Tap water.....	5.80	15	44	90
Nutrient.....	6.30	14	100

poor crops were obtained, not as a direct result of the H ion, nor because of free Al and Fe in the percolates, but simply because the soils lacked plant-food.

DISCUSSION

It seems to the writer that pH as a factor in plant distribution has been more assumed than proved. Although it is not denied that free acid is a toxic factor of itself when present in sufficient concentration, it still follows that pH is a poor criterion of the toxicity of a soil attributable to the H ion. Eliminating from the discussion the toxicity of Al and Fe apparent at low pH, there were at least two other important factors to be considered.

First: It is seen that distilled water itself is toxic to seedlings. True and Bartlett (12) and Osterhout (9), using different material, have demonstrated this. That there is a comparative toxicity is here shown. Phaseolus produces no growth after the first day whereas lupines continue development for at least

three. Such toxicity must be due to the absence of ions where one would expect the response of lupines to be more decided than the reaction of Phaseolus. That such is the case is shown in tables 2 and 3.

One value of pH as a criteria in plant distribution would be the possibility of predicting the p.p.m. total salts in the soil solution. K and Na salts are readily soluble at any acid concentration. Repeated cropping and leaching will in time deplete the soil solution. A fall in pH will follow. Magistad (8) shows that Ca is increasingly soluble with falling pH even in the presence of phosphates. Solubility tables indicate that Mg parallels Ca in this regard. One would expect in a virgin soil of pH 5.0 relatively little total Ca or Mg, and decreasing amounts are to be anticipated with increased cH.

Second: That plants must have Ca and respond variously to its presence has been recognized for many years. To quote from Warming (14)

certain plants are reputed to avoid soil containing much calcium carbonate, such as *Castanea sativa*, *Pinus maritima*, *Calluna vulgaris*, *Pteris aquilina*, *Rumex acetosella*, . . . ; also *Gramineae*, *Cyperaceae*, etc.—reputed to be incapable of carrying on existence in soil containing more than from 0.02–0.03 per cent CaCO_3 . But cultures—have clearly demonstrated that none of these plants suffer from lime when this is unaccompanied by a large amount of soluble salts. Other plants that do not desert a soil rich in CaCO_3 are—*Trifolium*, *Anthyllis*, *Rosaceae*, *Labiate*, many *Orchidaceae*, etc.

Warming's observations are based on the work of many European ecologists. The results in table 2, as far as they go, are in entire agreement. The response of species to the presence of various amounts of Ca would seem to be an important ecologic factor. That Phaseolus must have large amounts and that lupines attain maximum growth with relative traces are here shown. Experience suggests that peanuts require little Ca whereas the Cucurbits must have large amounts to insure significant growth.

The value of knowing the concentration of Ca in the soil solution is apparent from the consideration of the varied response of lupines and Phaseolus to this element. Whether pH is an adequate criterion of how much may be expected has not been adequately demonstrated. Further, the nature of the accompanying anion seems of some importance in this regard. True and Harvey (13) observe in part—

The Ca ion accompanied by the NO_3^- ion is from 4 to 5 times as favorable for absorption as the Ca ion accompanied by the SO_4^{2-} ion. The favorable effect of the NO_3^- and Cl^- ions is contrasted with the action of the SO_4^{2-} ion.

From a review of the literature, it seems difficult to determine the degree of toxicity of the H ion. The work of Kahlenberg and True (6) and Heald (5) indicates that the growth of *Lupinus albus* and *Zea mays* is apparently normal at a pH of from 3.8–4.3 with HCl , HBr , HNO_3 , and H_2SO_4 . The pH usually found in soils is not below 4.1 (15). Osterhout (10) shows that HCl antagonizes the ill effects of NaCl , decreasing the extent of leach and showing a beneficial action. But the work of Barratt (1) is most suggestive in this con-

sideration. This investigator shows that the pH of an acid solution is not the only criterion of how toxic that solution will be, but rather that the nature of the acid anion is a most important factor. Briefly, he found that 0.0001 *N* oxalic and lactic acids are lethal to *P. aurelia* in 9 minutes; that HCl, HNO₃, and H₂SO₄ are lethal in from 40–50 minutes; whereas it requires 85 minutes for acetic acid to kill.

From a consideration of the evidence presented, the writer suggests that pH determinations of any acid soil, with no other accompanying data, offer no adequate explanation of the type of vegetation found on that soil.

The behavior of radicals to free acid and to Ca suggests a permeability study which is being investigated with particular reference to the work of Hansteen-Cranner (4) and Clowes (3).

SUMMARY

Data are presented showing:

1. That with *Agrostis alba* var. in balanced nutrient solutions, growth is independent of pH within the limits 3.7–6.0,
2. That distilled water is more toxic to *Phaseolus* sp. than to *Lupinus albus*,
3. That in single salt solution, *L. albus* responds markedly to traces of Ca, deriving no additional benefit when the concentration exceeds 3.0 p.p.m., while *Phaseolus* does not respond significantly to concentrations of less than 5.0 p.p.m. of the same element, and that benefit is derived by increasing the concentration,
4. That *Phaseolus* will not survive a pH with HCl lower than 4.5, whereas a pH of 4.1 has little effect on lupines.

The antagonism of Ca for HCl is demonstrated.

Evidence is given suggesting that some soils of low pH are toxic to *Phaseolus*, not because of the toxicity of the H ion, but because of the absence of ions in the soil solution.

The data are discussed in support of the opinion that free acid in the soil as determined by pH measurements is not an ecologic factor only because of the toxicity of the H ion.

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THE PRECIPITATION OF CALCIUM OXALATE IN THE PRESENCE OF IRON, ALUMINUM, TITANIUM, MANGANESE, MAGNESIUM, AND PHOSPHATES, WITH SPECIAL REFERENCE TO THE DETERMINATION OF TOTAL SOIL CALCIUM¹

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It is well known that calcium oxalate can be precipitated in acid solutions, but its precipitation in the presence of iron, aluminum, titanium, manganese, magnesium, and phosphate, under conditions of acidity and ammonium chloride concentration sufficient to keep these other elements in solution, has not been very well worked out.

This work was undertaken in order to determine at what acidity calcium oxalate precipitates completely, and to ascertain whether under this condition, these other elements can be kept entirely in solution.

REVIEW OF OTHER METHODS

McCradden (3, 4) has proposed a method for the precipitation of calcium oxalate in acid solutions in the presence of magnesium and phosphates. Excellent results have been reported by Mitchell (5) and Patten (6) when the exact conditions of this method were employed.

Winkler (10), Ewe (2), and Congdon (1) have summarized and reported results obtained by using various methods for determining calcium. Calcium oxalate precipitated in slightly acid solutions is entirely accurate according to their findings.

Shohl (8) has shown from a theoretical consideration of the solubility products of the possible precipitates in a calcium, magnesium, phosphate, and ammonium mixture, that calcium should precipitate completely and alone as the oxalate at pH 4.0. This he finds can be accomplished experimentally.

Stoker (9) found that the occlusion of magnesium in the calcium oxalate precipitation could be reduced to 0.06 per cent by allowing calcium oxalate to precipitate incompletely at first in a boiling solution at pH 0.7 to 1.0 and then bringing it gradually to neutrality.

Shedd (7) has proposed a method for determining total calcium in soils.

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Calcium oxalate is precipitated in a solution faintly acid with HCl, in the presence of iron, aluminum, magnesium, manganese, and phosphorus. Manganese presumably precipitates along with calcium, however, and is removed by dissolving the filtered calcium and manganese in acid and precipitating manganese with bromine. The calcium is then reprecipitated by ammonium oxalate and weighed as CaO.

Two improvements in this method seem possible: first, the regulation of acidity by means of indicators; and, second, the possibility of holding manganese in solution, avoiding thereby this extra step in Shedd's procedure.

TABLE I
Precipitation of calcium oxalate at different H-ion concentrations

NUM-BER	INDICATOR USED	COLOR	pH	HIGH CALCIUM		MEDIUM CALCIUM		LOW CALCIUM	
				Taken	Recov-ered	Taken	Recov-ered	Taken	Recov-ered
				mgm.	mgm.	mgm.	mgm.	mgm.	mgm.
A	Phenol	Red	7.6	32.10	32.10	8.05	8.05	1.51	1.51
B	Red	Red	7.4	32.10	32.10	8.05	8.05	1.51	1.51
A	Brom cresol	Light blue	6.0	32.10	32.20				
B	Purple	Yellow	5.6	32.10	32.10				
A	Brom cresol	Yellow green	3.8	32.10	32.10	8.05	8.05	1.51	1.51
B	Green	Light green	3.9	32.10	32.20	8.05	8.00	1.51	1.51
A	Brom phenol	Greenish blue	3.8	32.10	32.10				
B	Blue	Yellow	3.6	32.10	32.20				
A	Thymol	Pinkish yellow	2.3	32.10	31.90				
B	Blue	Light Red	2.2	32.10	31.90				

CONDITIONS UNDER WHICH SINGLE ELEMENTS PRECIPITATE

Calcium

It was thought desirable to determine first at what pH calcium oxalate precipitates completely. A standard CaCl_2 solution was made from calcite.

Various indicators were used to determine the desired pH and the color changes were checked up electrometrically.

The calcium to be precipitated was made to a volume of 150 cc. in which 10 drops of 0.04 per cent indicator, 2 gm. of oxalic acid, 4 gm. of NH_4Cl , and 10 cc. of 1.76 N acetic acid were dissolved. Acetic acid prevents the solution from becoming more acid upon digestion, as is the case when only oxalic acid is present. The solution was brought nearly to boiling and 5 N ammonia added until the desired color changes were reached. The calcium precipitate was boiled gently a few minutes, digested on the steam bath for 2 hours, and then

allowed to stand over night. The pH at this point was determined by the quinhydrone electrode on a sample of the supernatant liquid. The precipitate was filtered, washed, dissolved in 4 N H₂SO₄, and titrated with standard KMnO₄. Three concentrations of calcium, representing somewhat the range of calcium which will be found in soils, were employed. The results obtained are recorded in table 1.

The results show that calcium precipitates completely at an acidity at least as low as pH 3.6. At pH 2.3 there is some slight solubility. Since complete precipitation occurs at pH 3.9 in all concentrations studied, and since pH 3.9 to 4.2 is the turning point of brom cresol green from yellow to green, it was decided to try out the solubility of manganese, magnesium, iron, titanium, aluminum, and phosphorus alone and combined at this acidity.

TABLE 2
Conditions under which iron precipitates

NUM-BER	INDICATOR	COLOR	pH	COMPLETE SOLUTION		NO OXALIC ACID	
				0.2 gm. FeCl ₃	0.5 gm. FeCl ₃	0.2 gm. FeCl ₃	0.5 gm. FeCl ₃
1	Phenol red	Red masked some by Fe.	7.4	Precipitate	Precipitate	Precipitate
2	Brom cresol purple	Yellowish green	5.8	No precipitate	Precipitate	Precipitate
3	Brom cresol green	Distinct green	4.2	No precipitate	No precipitate	Precipitate	Precipitate
4	Brom phenol blue	Light green	3.7	No precipitate
5	Thymol blue	Yellow	2.4	No precipitate

Manganese

A standard solution containing 0.243 gm. of manganese per liter was made up from manganese di-chloride.

Ten cubic centimeters of standard were made up to 150 cc. using the same amounts of oxalic acid, ammonium chloride, and acetic acid as were used for the calcium. The same precipitating procedure as used for calcium was followed. One sample was brought to pH 7.08 and the other to pH 4.2. After standing over night, inspection failed to reveal any sign of precipitate. When the same series were run omitting NH₄Cl, manganese oxalate precipitated.

Iron

In order to determine the conditions under which iron can be kept in solution, the following tests were made: Two concentrations of FeCl₃, as indicated in table 2, were made up to 150 cc., one set containing the same reagents as

used for calcium, the other set omitting oxalic acid. The same precipitating procedure as used for calcium was followed and notes were taken as to the presence of a precipitate. The results are given in table 2.

Only at pH 7.4 in the presence of oxalic acid did iron precipitate. At higher acidities no precipitation occurred. The color changes of indicators are somewhat different in the presence of iron. Brom cresol green becomes distinctly green as the H-ion concentration is decreased, and its blue color does not develop so readily.

In the absence of oxalic acid, iron precipitates in an acid solution at pH 4.2 and will probably precipitate at acidities higher than this.

Aluminum

A solution containing 0.2 gm. of AlCl_3 and the same reagents as employed in the calcium determination, was carried through the same procedure as for the precipitation of calcium.

No precipitation occurred at pH 4.0.

TABLE 3
*Precipitation of magnesium from oxalate solutions**

NUMBER	pH	MAGNESIUM PRECIPITATE	
			mgm.
1	4.2	.	1.21
2		.	2.57
1	3.6	.	2.95
2		.	2.00

* 78 mgm. of magnesium in solution.

Magnesium

Magnesium chloride was made up from C. P. recrystallized MgCl_2 . Its precipitation in oxalate solution at pH 4.2 and 3.6 was tried out using various concentrations of magnesium.

In the first series, a solution containing 78 mgm. of magnesium was made up to 150 cc. The same amounts of NH_4Cl , oxalic acid, and acetic acid as used for the calcium determination were added. A precipitate was found after the solution had stood over night. The amount of magnesium precipitated was determined by titration with KMnO_4 . The results are recorded in table 3.

Appreciable amounts of magnesium precipitated under these conditions. Two solutions were made up containing 31.2 and 7.8 mgm. of magnesium, respectively, and the usual precipitation procedure was followed. No precipitation occurred in either case and since the former amount represents the approximate limits of magnesium usually found in 1-gm. samples of humid soils, no further experiments relative to the amounts of NH_4Cl and oxalic acid necessary to keep higher concentrations in solution were carried out.

Titanium

A solution of titanium sulfate containing the equivalent of 1.0 mgm. TiO_2 per cubic centimeter was made up by fusing TiO_2 with KHSO_4 . Ten cubic centimeters of this solution was brought to a volume of 150 cc. in which brom cresol green indicator, acetic acid, oxalic acid, and ammonium chloride in the same concentration as used for the calcium precipitation were dissolved. No precipitation occurred at pH 4.0. When made more alkaline, however, a precipitate forms. This precipitate, however, is not an oxalate but a hydrated titanic acid and, therefore, in the permanganate determination of calcium would be harmless.

PRECIPITATION OF CALCIUM OXALATE AT pH 4 IN THE PRESENCE OF IRON, ALUMINUM, MAGNESIUM, PHOSPHORUS, AND MANGANESE

A synthetic solution containing iron, aluminum, calcium, magnesium, and manganese as the chlorides, and phosphorus as sodium phosphate, representing

TABLE 4
Precipitation of calcium oxalate in the presence of Fe, Al, Mg, Mn, and P

NUMBER	COMPOSITION OF SOLUTION	pH	CALCIUM
			mgm.
1	Calcium alone	4.0	8.04
2	Calcium alone	4.0	8.04
3	Complete solution	4.0	8.13
4	Complete solution	4.0	8.18
5	Complete solution	4.0	8.23

somewhat the amounts of these various constituents which might be found in a soil, was prepared. The amounts contained in the solution with what these would represent in soil percentages are given below:

	gm. in solution	equivalent to per cent in soil
Al_2O_3	0.05	5.00
Fe_2O_3	0.05	5.00
Ca.....	0.00805	0.85
Mg.....	0.0078	0.78
MnO	0.0051	0.51
P_2O_5	0.001	0.10

Aluminum may be somewhat low on the average. Magnesium, manganese, and phosphorus are somewhat high in comparison to what is usually found in Wisconsin soils.

Precipitation was carried out at pH 4 in a boiling solution containing 4 gm. of NH_4Cl , 2 gm. of oxalic acid, 10-cc. of 1.73 N CH_3COOH , and 10 drops of 0.04 per cent brom cresol green. The results are recorded in table 4.

It appears that a slight amount of magnesium perhaps co-precipitates in the presence of calcium. It was thought that this slight co-precipitation of magnesium could be prevented by increasing the NH_4Cl concentration, and decreasing the oxalic acid concentration. A second series containing 6 gm. of NH_4Cl and 0.5 gm. of oxalic acid was precipitated as before. The results are given in table 5.

These results indicate that magnesium in the concentration used in this solution can be kept from precipitating if sufficient NH_4Cl and not too great an excess of oxalic acid are used.

COMPARISON OF THE STANDARD AND THE PROPOSED METHOD FOR DETERMINING TOTAL CALCIUM IN SOILS

In order to try out the method on soils, total calcium was determined by the standard method and by this method. In the standard method, silica was removed by dehydration, iron and aluminum removed by precipitation with NH_4OH , manganese removed by precipitation with bromine, and calcium determined by precipitation with oxalic acid solution following the directions

TABLE 5
Precipitation of calcium oxalate in the presence of Fe, Al, Mg, Mn, and P

NUMBER	COMPOSITION OF SOLUTION	pH	CALCIUM
			mgm.
1	Calcium alone	4.0	8.13
2	Calcium alone	4.0	8.13
3	Calcium alone	4.0	8.13
4	Complete solution	4.0	8.09
5	Complete solution	4.0	8.09
6	Complete solution	4.0	8.13

of standard methods. The double precipitation procedure for calcium was followed.

In the proposed method, silica was removed as usual and the filtrate made up to 200 cc. Six grams of ammonium chloride, 1 gm. of oxalic acid, 10 cc. of 1.76 N acetic acid, and 10 drops of 0.04 per cent brom cresol green were added to the cold solution. It was brought nearly to boiling, and 5 N ammonia added slowly until the solution changed from yellow to the first distinct green. It was then boiled for a few minutes in order to precipitate calcium oxalate in granular form.

The precipitate was allowed to stand over night. Calcium was determined by the permanganate method. Blanks were run in both sets. The results are as follows:

<i>Total Calcium in Soil 323</i>		
	<i>Standard Method</i>	<i>Proposed Method</i>
1.	0.857 per cent	1. 0.867 per cent
2.	0.862 per cent	2. 0.876 per cent

A slightly greater amount of calcium was obtained by the proposed method, but the difference is small and within the range of experimental error, and because of the shortened procedure is doubtless more nearly correct than calcium determined by the standard method.

Since excellent results can be obtained in the presence of amounts of iron, aluminum, manganese, magnesium, and titanium as found in soils, it is obvious that on soil extracts obtained by various solvents, this determination offers convenience and rapidity.

METHOD ADOPTED

The method adopted for the determination of calcium in all soils and soil extracts is as follows:

To the solution containing calcium, magnesium, manganese, iron, aluminum, titanium, and phosphorus, is added enough ammonium chloride to insure the presence of at least 6 gm. If the solution is acid with HCl, as is often the case, the amount present is calculated approximately and the required amount of ammonium chloride added. One gram of oxalic acid in solution, 10 cc. of 1.76 N acetic acid, and 10 drops of 0.04 per cent brom cresol green are added. The solution is made to a volume of 150 to 200 cc. and brought nearly to boiling. Dilute ammonia is added slowly until the color changes from yellow through yellowish green to the first pure green. The solution is then boiled gently for 5 to 10 minutes, the calcium precipitating in a coarse crystalline state. The precipitate is then allowed to stand on a steam bath until it wholly subsides. The precipitate should be allowed to stand at least three hours to insure complete precipitation. In determining calcium by titration with permanganate, the precipitate should be washed as few times as possible with distilled water, for calcium oxalate is slightly soluble. Using 9 cm. no. 589 S & S paper, it has been found for all ordinary amounts of calcium oxalate that rinsing the beaker three times, plus washing the precipitate five times, removes all excess oxalate.

SUMMARY

1. Experimental work has been reported showing that it is possible to precipitate calcium oxalate completely and alone at pH 4.0, in the presence of iron, aluminum, titanium, manganese, magnesium, and phosphates.
2. This method as worked out is applicable to the determination of total calcium in soils, soil extracts, and plant tissue, and under other conditions where the proportion of these various elements occur in somewhat similar amounts as used in the experimental work recorded.

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